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Technical Manual for the Analysis of Fuels

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16. ABSTRACT The manual is for use as a guide in research projects concerned with fuel combustion. Basically, it describes and discusses standard methods of sampling and analysis for a variety of hydrocarbon fuels. The analyses covered are those of prime concern to the combustion engineer; no attempt is made to cover all analyses that may be required in a complete environmental assessment of any fuel combustion process. For each fuel covered, the manual indicates the analyses that are likely to be required the preferred method of analysis, and available sampling procedures. For each method of analysis listed (preferred plus alternates, in many cases), the manual summarizes the method, discusses its applicability, and describes its precision. The manual covers gaseous fuels, liquid petroleum fuels, waste lubricating oil, shale oil, coal liquids, methyl fuel, coal, coke, refuse-derived solid fuels, and peat. The appendices give: the availability of Standard Reference Materials for fuel-related analyses; laboratory directories; typical values (or ranges) of parameters specified for each fuel; and results of fuel analyses conducted by the contractor.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Methodology	Pollution Control	13B	
Hydrocarbons	Petroleum Products	Stationary Sources	07C	11G
Fuels	Fuel Oil	Gaseous Fuels	21D	11H
Combustion	Shale Oil	Waste Lubricating Oil	21B	08G
Analyzing	Wastes	Refuse-Derived Solid Fuel	14B	
Sampling	Carbinols			
Coke, Coal	Peat, Refuse			

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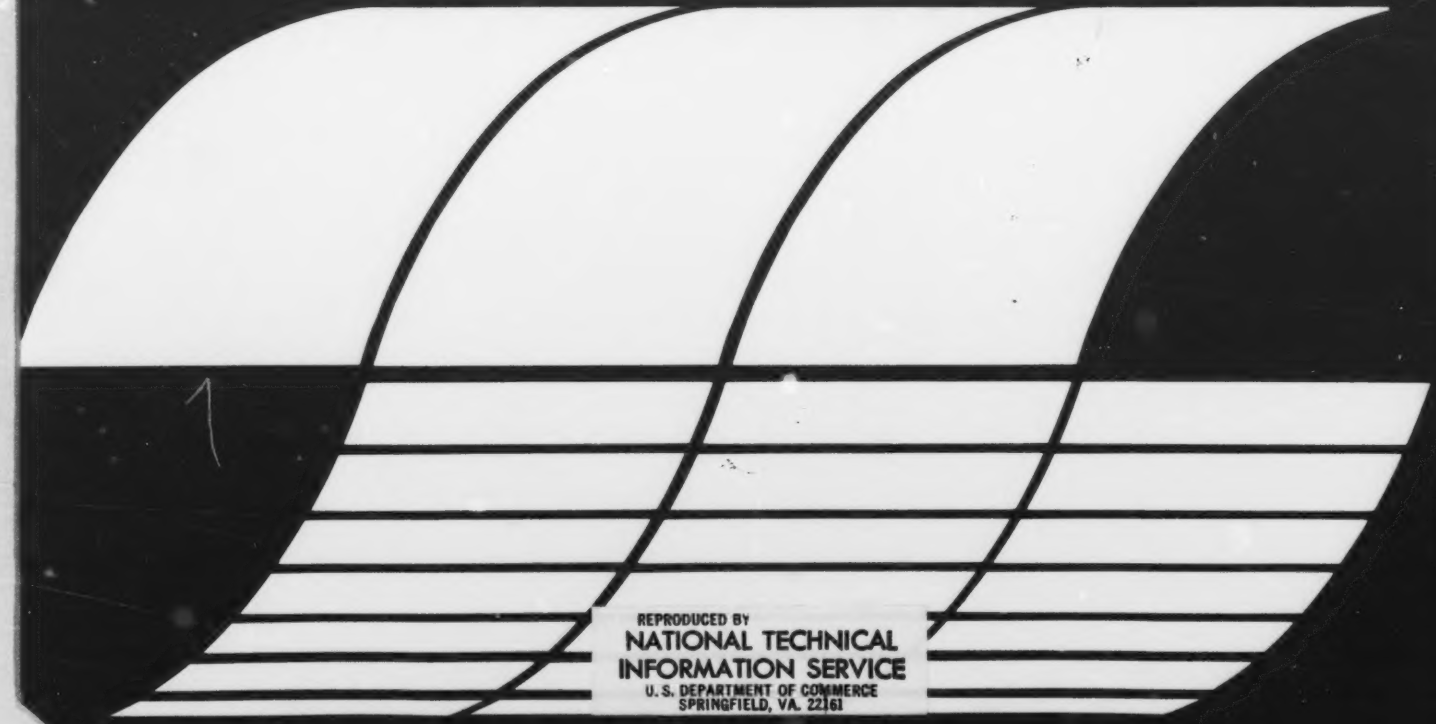

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TECHNICAL MANUAL FOR THE ANALYSIS OF FUELS

by

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CHAPTER I

INTRODUCTION

1. OBJECTIVES

This manual is intended for use as a guide to fuel sampling and analysis in IERL/RTP projects concerned with fossil fuel utilization. The information given is basically a description and discussion of established methods of sampling analysis for a variety of hydrocarbon fuels. The analyses covered are those that are of prime concern to the engineer, or project director, involved in a pollution related research project.

The coverage of non-standard methods and of additional parameters that may be required in environmental assessments will be included in a forthcoming Level 2 sampling and analysis manual. The non-standard methods will include, for example, those that are state-of-the-art or that use rapid instrumental techniques. The parameters added will be those yielding information on the chemical nature of the fuel (e.g., classes of organic chemicals), trace element composition, or certain additional physical properties.

This manual indicates what fuel analyses are normally required in connection with fuel-utilization research, and what established methods are applicable for the analysis. If this manual serves only to point out the importance of methods specification in fuel analysis, it will have been of value. Too frequently, analyses of samples - including fuels - result in inaccurate or meaningless results because an inappropriate method was used. It should not be assumed by the researcher or project director that the analytical laboratories (Government or private) will use the method that is both appropriate and standard. It is, unfortunately, easy to make this assumption, in part because methods published by one organization, the American Society for Testing and

Materials (ASTM), are so widely recognized and used. There are, however, a large number of ASTM methods available for various fuels, including two or more alternative methods for many parameters, and the choice of the most applicable method is important. In addition, many standard methods, including some ASTM methods, leave certain options to the parties concerned - e.g., the temperature or pressure at which a test is to be made. If the researcher or project director does not specify the options to be used, the laboratories may run the test in an inappropriate manner.

2. GENERAL RECOMMENDATIONS

Upon questioning, analytical laboratories conducting fuel analyses are likely to give statements such as: "We follow ASTM methods or the equivalent"; "Generally use ASTM or a closely related method"; "Follow ASTM almost entirely". It is recommended that, such statements aside, the exact method of analysis be specified for every parameter by the researcher or project director. In many cases, the method chosen will be one that is routinely carried out by the laboratory, and this is a desirable feature. If the laboratory indicates that it normally uses a different method for one or more of the parameters, then a determination must be made on the applicability of the method and the desirability of its use. One area where such determinations may be frequently required is that of instrumental methods for carbon, hydrogen, and nitrogen analyses. If the method normally used with the instrument is applicable for the fuel in question, then it may be desirable to use that instrumental method since it may result in time and cost savings. If a large number of samples are to be analyzed by any such non-standard method, then steps should be taken to check both the accuracy and precision of the method.

Five additional recommendations are: (1) that the laboratory be required to specify the exact method of analysis (and any modification) used on samples for a given report; (2) that the laboratory be required to state the detection limits of the method (or instrument) used for any result that is near or below the detection limit; (3) that the precision of the results be included in all reporting; (4) that the parties concerned agree, in advance, on the basis for reported results (e.g., "as-received" versus "moisture-free" for fuel containing water) if it is not specified by the chosen method; and, (5) for any large sampling and analysis program that the laboratory be required to submit information on its quality control procedures, including the results of any tests carried out (e.g., blanks, standards, duplicate results) during the course of the program.

3. CONTENTS OF THE MANUAL

For each fuel covered, the manual indicates what analyses are likely to be required, and what method(s) and analysis and sampling procedures are available. For each method of analysis listed - preferred plus alternates in many cases - the manual gives a summary of the method, a discussion of its applicability, and information on the accuracy and precision of the method, if known. The main emphasis is on methods of analysis; sampling methods are, in general, only discussed briefly.*

The listing in this manual of an analytical method as "preferred" method does not mean that it is the only acceptable method, or even that it is the best from an analytical standpoint. What is implied is a recommendation over the other available methods based on considerations of applicability, precision and accuracy, availability of detailed instructions, and current or expected usage. The criteria for the selection of methods to be included in this manual, and for the selection of "preferred" methods, are given in the following subsection.

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*For additional guidance in sampling, the reader should refer to "Technical Manual for Process Sampling Strategies for Organic Materials," U.S. Environmental Protection Agency, Research Triangle Park, Durham, North Carolina; April, 1976. (EPA-600/2-76-122, NTIS Report PB 256-696/AS.)

The analyses listed for each fuel may not meet the information needs of all research projects, nor is the listing intended to be a maximum or minimum set of analyses. For a given research project, the parties concerned should use the given list as a starting point and then add or subtract parameters as the program's informational needs dictate.

The fuels covered in this manual are: gaseous fuels, coal and coke, coal liquids, shale oil, liquid petroleum fuels (broken into several categories), waste lubricating oil, methyl fuel, refuse-derived solid fuel (from municipal refuse), and peat. Not all of the fuels covered are in commercial use, at present. These unconventional fuels were included, however, because of their likely use in the future and the need, therefore, for research programs to be carried out on them.

Each subsequent chapter of this manual covers a fuel or fuel grouping. The introduction to each chapter defines the fuels being discussed, indicates the analyses covered (and the preferred method of analysis), and gives other supplemental information about the fuel that may be of interest in any environmental assessment of processes using the fuel. A section on sampling is given and is followed by the main section describing the methods of analysis. References for each chapter are given at the end of the text portion of that chapter.

Appendices give (1) information of the availability of Standard Reference Materials for fuel-related analyses; (2) a listing of laboratory directories; (3) typical values (ranges) for the parameters specified for each fuel; and, (4) the results of fuel analysis tests conducted by the contractor and three analytical service laboratories.

4. CRITERIA FOR METHODS SELECTION

The criteria used in the selection of the preferred and alternate methods of analysis involved the following considerations:

1. Applicability of the method to the fuel in question;
2. The accuracy and/or precision of the method;
3. The availability of the publication containing the method and the extent to which the method is currently used in laboratories conducting fuel analyses.

The considerations listed in #1 and #2 were dominant in most instances. No attempt was made - in the preparation of this manual - to review all available methods because of limitations on time and funds. If a particular method was deemed applicable and "available", then it was considered. No method was considered for inclusion in this manual unless it had been reported in sufficient detail in the open literature. Additionally, no attempt was made to resolve, by laboratory tests, the numerous uncertainties concerning the applicability of specified methods to fuels other than those the method was originally intended for. Some laboratory tests on unconventional fuels were carried out as part of this program (see Appendix D), but the scope of these tests was insufficient to make a defensible decision on the applicability of the method used.

CHAPTER II

GASEOUS FUELS

1. INTRODUCTION/SUMMARY

Gaseous fuels are mixtures of vapor-phase species including low molecular weight hydrocarbons (up to and including small amounts of C_7 compounds), carbon oxides, nitrogen, hydrogen, helium, sulfur compounds (hydrogen sulfide and/or mercaptans), and oxygen. Fuels from different sources have rather different compositions as, for example:

Natural Gas - methane is major component with lesser amounts of saturated hydrocarbons, trace amounts of sulfur compounds and air components, no carbon monoxide[1].

Industrial Gas (coal gasification) - carbon monoxide and dioxide, some hydrocarbons (but little methane), nitrogen, minor amounts of sulfur compounds[2,3].

The relatively small number of compounds possible in gaseous fuels has resulted in the development of methods for the identification and measurement of individual major and minor components using either gas chromatography or mass spectrometry. While standardized procedures for such measurements have been established, continuing improvements in instrumentation and chromatographic column technology have resulted in modified procedures which allow the analyses to be carried out more quickly and conveniently with no loss in precision or accuracy. Laboratories which are very active in the area of gas analyses often develop and utilize procedures and equipment based upon these modifications and improvements before such improvements have been incorporated into standards such as the ASTM methods.

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Table II-1 presents a summary of analyses for gaseous fuels along with the preferred methods. Section 3 of this chapter provides additional information on analytical procedures, as well as alternate methods. The preferred methods have all been selected from the American Society for Testing and Materials (ASTM) methods for gaseous fuels[1]. A more complete listing and description of methods applicable to the various composition and physical property parameters is given in Table II-2.

2. SAMPLING

Methods for sampling gaseous fuel streams will vary according to the pressure, temperature, and content of reactive gases (such as H_2S) of the particle stream. Pressure in natural gas streams, for example, may vary from several thousands of pounds at the well-head and some transmission lines down to a few inches of water in service feed lines. In some industrial applications where the gasification process equipment is close to the end use, gases may be at temperatures above ambient.

General directions for sampling natural and manufactured gases at low temperature and low pressure are covered in ASTM D 1145, "Standard Method of Sampling Natural Gas"[1], and ASTM D 1247, "Standard Method of Sampling Manufactured Gas"[1], respectively.

Grab samples representative of the gas stream at one point in time are generally taken, although continuous, integrated samples can be obtained by use of a slow, regulated flow into a large sample container.

In sampling from a pipe, or other vessel, it is generally good practice to use a sampling probe, or tip, which protrudes some distance into the vessel and away from the wall, in order to avoid any effects of condensation or reaction at the wall which might alter the composition of the sample being taken.

A more general approach to sampling gaseous products from coal gasification processes has been described by TRW[2]. In some cases, the product fuels may be hot and may still contain some amounts of sulfur compounds, higher hydrocarbons, and ammonia which have not been removed.

3. ANALYSIS METHODS

Table II-2 gives a more complete description of methods applicable to each parameter. When more than one method is available, the preferred method is listed first. The parameters are listed in that same order as in Table II-1.

The principal methods for measurement of major constituents in gaseous fuels are gas chromatography and mass spectrometry. Gas chromatography is a very powerful technique for separation and measurement of complex mixtures. However, this technique is dependent upon the availability and use of reference standard gas mixtures for empirical calibration of quantitative and qualitative (i.e., chromatographic retention time) response. For best results, these calibration mixtures should be reasonably close in composition to the sample(s) of interest.

Mass spectrometry affords qualitative identification of major components. With the use of suitable reference standards, it can give more quantitative information as well as provide further identification.

Because of the varying need for standards, initial analysis of a completely unknown gaseous fuel should probably be done using mass spectrometry. Once an approximate composition is known, then gas chromatography, with appropriate standards, can be used for subsequent analyses.

The estimates of precision given in Table II-2 are drawn largely from ASTM studies. The accuracy of these measurements is, for the most part, a function of the accuracy with which the calibration standards have been made. In addition, for the methods which involve consumption or reaction of large volumes of sample, the accuracy of the measurement will also be a function of the state of the volume measurement apparatus.

Measurement of the calorific value and density of isolated (i.e., small volume) samples of gaseous fuels is not often done. Instrumentation for such measurements is really designed for continuous operation, and requires relatively large volumes of sample to reach stable operation. Calculations of both calorific value and density, based upon the composition data from gas chromatography and mass spectrometry, is now done frequently as part of the gas analysis[5,6].

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.
2. Hamersma, J. W. and Reynolds, S. L., "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," TRW Systems, U. S. Environmental Protection Agency Contract No. 68-02-1412, Task Order No. 3, March, 1975.
3. Tillman, D. A., "Status of Coal Gasification," Environmental Science Technology, Volume 10, pages 34-38, 1976.
4. Purcell, J. E., Gilson, C. P., "Improved Analysis of Natural Gas," Chromatrography Newsletter, Volume 1, pages 45-50, 1972.
5. Private communication with Mr. James Baratta, Washington Gas Light Company, Arlington, Virginia, April, 1977.
6. Private communication with Mr. Louis Molinini, Gollob Analytical Service Corporation, Berkeley Heights, New Jersey, April, 1977.
7. "Annual Book of ASTM Standards (1974) - Part 24: Petroleum Products and Lubricants (II)," American Society for Testing and Materials, Philadelphia, Pennsylvania.

Table II-1

ANALYSES FOR GASEOUS FUELS

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (ℓ)	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Natural Gas Components	ASTM D 1137	∿ 0.3	100	G-1
2. Gasification Process, Components	ASTM D 1946 (or modification thereof)	∿ 0.3	150 - 250	G-2 special
3. H_2S[e]	ASTM D 2725	3[e]	30	G-2 special
4. Total Sulfur Compounds	ASTM D 1072	30[e]	50	G-2 special
5. Calorific Value	By calculation from components in ASTM D 1137 and ASTM D 1946 above; or ASTM D 1826 (continuous gas calorimeter)	100	Not known	G-3

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a. All ASTM methods are given in References #1 and #7.

b. These are the sample requirements for a single analysis. Approximate Amount of Sample Needed for Analysis = Volume (STP) of Sample Required for Analysis.

c. Estimated based on prices charged by analytical service laboratories in early 1977.

d. See Appendix A, Table A-1 for Standard Reference Materials available.

e. There is some question regarding the stability of such samples in sampling containers. Where possible, the samples should be taken and treated at the source. If this is not possible, the appropriate inert (e.g., glass) sample containers should be used.

Table II-2

METHODS OF ANALYSIS FOR GASEOUS FUELS

	SUGGESTED METHOD(S)				
PARAMETER	No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
1. Natural Gas: Components	A. ASTM D 1137	1	A portion of the gas sample is subjected to mass spectroscopic analysis. The mass spectrum of the mixture is analyzed by comparison with the spectra of individual, pure components of the mixture.	Natural gases, including saturated hydrocarbons to C_6, carbon oxides, in hydrogen sulfide, C_1-C_2, mercaptans; minimum level for measurement is 0.1% in mixture.	(P) The expected precision (95% confidence) for the analysis of natural and synthetic gases over a range of concentrations is: Conc. Range / Individual Analyst / Between Labs 0% - 1% / 0.1 / 0.1 - 0.2 1% - 5% / 0.1 / 0.2 - 0.4 5% - 25% / 0.1 - 0.3 / 0.3 - 0.9 > 25% / 0.2 / 0.5 - 2. The variations in precision result from different studies; in general analyses of natural gas give better precision than those of synthetic gases.
	B. ASTM D 1945	1	Individual constituents are separated by gas chromatography on a column suitable for the required separation, and are measured by means of a thermal conductivity detector. Constituent identification and quantitative calibration are accomplished by analyzing reference standard gas mixtures under same conditions.	O_2, N_2, CH_4 - uses molecular sieve column. CO_2, C_2-C_6 hydrocarbons uses partition column of silicone oil or other absorbants. Can also be used for separation of some synthesis gases.	(P) Reproducibility: The expected precision (95% confidence) over the range of concentrations is: Conc. Range / Individual Analyst / Between Labs 0% - 1% / 0.03 / 0.06 1% - 5% / 0.05 / 0.1 5% - 25% / 0.15 / 0.2 > 25% / 0.30 / 0.6 Heavy (C_6) fractions / 5% of amount / 10% of amount

All notes appear on the last page of this table.

Table II-2

METHODS OF ANALYSIS FOR GASEOUS FUELS

(continued)

PARAMETERS	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)
	No./Title	Ref.			
1. Natural Gas: Components (continued)	C. ASTM D 1945 (Variations of)	4	Variations of D 1945 include the following modifications: a. Use of smaller columns with different liquid substrates b. Use of porous polymer column packing c. Use of temperature programming	Each of the variations has been applied to analysis of natural gas.	(P) Relative standard deviations range from 0.1% to 4% for major to trace (0.05%) hydrocarbons.
2. Synthetic Gas: Components	A. ASTM D 1946	1	Method similar to that for natural gas (D 1945) except that different chromotographic columns used to afford separation of large amounts of carbon monoxide, nitrogen, and unsaturated hydrocarbons often found in synthesis gases.	Column packing and length modified as necessary for particular mixture.	(P) See information given in #1 (Natural Gas), Part C.
	B. ASTM D 2650	7	Method basically the same as for natural gas. See #1 (Natural Gas), Part A.	Applicable to mixtures of saturated and unsaturated hydrocarbons, and carbon monoxide.	(P) See information given in #1 (Natural Gas), Part A.
3a. Hydrogen Sulfide	ASTM D 2725	1	Hydrogen sulfide is scrubbed from the gas stream with zinc acetate solution. The sulfide is treated with acidified solution of an aromatic amine and ferric chloride catalyst to form methylene blue due which is measured by colorimetry.	Applicable to gases containing up to 23 mg H_2S/cu meter. Limit of method is .023 mg H_2S. Should be applicable for all synthesis gases.	(P) The repeatability (individual analyst - 95% confidence) over the range of applicability (in mg/cu meter) is: Sulfide Conc. Range — Repeatability < 1% — 0.2 1% - 5% — 0.4 5% - 23% — 10% of amount

Table II-2

METHODS OF ANALYSIS FOR GASEOUS FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHOD	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
3b. Hydrogen Sulfide and Mercaptan Sulfur	ASTM D 2385	7	Hydrogen sulfide is scrubbed from the gas stream with neutral cadmium sulfate solution, and mercaptans with alkaline cadmium sulfate solutions. Sulfide and mercaptans are measured by iodometric titration.	Applicable to gases containing up to 100 mg H_2S/cu meter and 22 mg mercaptan S/cu meter. Limit of method is 20 mg. Method should be applicable for any synthesis or reformer gas. Sample should be collected at the source.	(P) The precision (95% confidence) over the range of applicability (in mg/cu m) is: Sulfide Conc. — Expected Precision (mg/cu m): Individual — Labs 2.3 — 0.7 — 0.9 23 — 2.5 — 3.4 115 — 8.2 — 11.4
4. Total Sulfur	A. ASTM D 1072	1	Sample is burned in closed system and sulfur oxides are absorbed (as sulfate) into sodium carbonate solution. Sulfate is titrated with barium chloride solution to a color indicator endpoint.	Applicable to gases containing 23 mg S/cu meter to 700 mg S/cu meter.	(A) Accuracy expected to be from 2 mg S/cu m to 16 mg S/cu m. (P) No precision data.
	B. ASTM D 3031	1	Sample is combusted in hydrogen to hydrogen sulfide and measured by the methylene blue method.	Applicable to gases containing up to 23 mg S/cu meter, and not more than 0.5% of C_5 and heavier hydrocarbons.	(P) The expected precision (95% confidence) over the range of applicability (in mg S/cu m) is: Sulfur Conc. Range — Repeatability < 1% — 0.2 1% - 5% — 0.4 5% - 23% — 10% of amount
5. Calorific Value	ASTM D 1826	1	A known flow of gas is burned and the heat transferred to a known air flow. The temperature of the air is then related to the calorific value.	Applicable to gases in the 8,000 K cal to 11,000 K cal/cu meter (900 Btu to 1,200 Btu/cu foot); apparatus can be adjusted for gases of lower calorific value.	(P) With weekly standardization precision (95% confidence) expected to be 0.3% or better.

Notes for Table II-2:

*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference of duplicate results submitted by two or more laboratories. The original reference should be checked if precision is critical since the wording may imply special conditions for the applicability of the precision numbers given.

CHAPTER III

LIQUID PETROLEUM FUELS

1. INTRODUCTION/SUMMARY

Liquid petroleum fuels include all the fractions commonly isolated from the distillation of crude oil and are listed below in order of decreasing volatility.

1. Liquefied petroleum gas
2. Gasoline (motor and aviation)
3. Gas turbine fuels
4. Diesel fuels
5. Heating oils

The discussion also deals with waste lubricating oils which are sometimes combusted. Table III-1 gives a summary listing of the fuel analyses that are important for liquid petroleum fuels combustion, along with an identification of the preferred method of analysis. Quantities of the sample required, costs, and standard reference materials (where available) are given in Table III-2. Additional information on the methods of analysis is tabulated in Section 3 of this chapter. All of the methods discussed are taken from the American Society for Testing and Materials' (ASTM) standards for petroleum products and lubricants[1].

A complete environmental assessment of processes using certain liquid petroleum fuels will require analyses beyond those covered by this manual; for example, analysis of trace metals in heating oils and waste lubricating oils, analysis of hydrocarbon components such as polunuclear aromatics in heavy heating oils, and stability to oxidation.

Petroleum fuels consist mainly of hydrocarbons which increase in molecular weight and structural complexity from liquefied petroleum gas to heating

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oils. The fuels are specified according to physical and use-related parameters and, therefore, may differ in chemical composition from sample to sample.

Nitrogen, sulfur, and trace metals are only present in trace quantities in the lighter fuels, i.e., up to gas turbine fuels or light heating oils[2]. The heavier heating oils contain higher amounts of nitrogen, sulfur, and trace metals because processing of the crude oil concentrates these materials in the heavier fractions. Performance specifications for gasoline, diesel oil, and gas turbine fuels strictly limit the amounts of these impurities which may be present. However, some of the fuels may contain additives, e.g., lead alkyl compounds are added to gasoline to improve its anti-knock properties. Waste lubricating oils may contain a variety of added components such as phosphorus, zinc, calcium, and barium.

Petroleum fuels may be subjected to long periods of storage, and additives (e.g., sulphonates, amines, metal phenolates) are used to inhibit oxidation.

Sulfur is present as mercaptans, sulfides, and thiophenes. Nitrogen is found as derivatives of pyridine and pyrole. Oxygen compounds are quinones, phenols, and acids.

2. SAMPLING

Procedures for sampling liquid petroleum fuels are given in ASTM D 270, "Standard Method of Sampling Petroleum and Petroleum Products"[1]. This standard describes the various types of sampling procedures and sampling containers to be used for different liquid petroleum fuels. Liquefied petroleum gas (LPG) must be sampled in a different manner because of its high volatility at room temperature. ASTM D 1265 describes the "Standard Method of Sampling Liquefied Petroleum Gases"[1].

3. ANALYSES

Table III-3 gives, for each parameter of interest, additional information on the method(s) of analysis deemed suitable. When more than one method is listed, the preferred method is listed first. The parameters are listed in the order given in Table III-1.

Most of the methods described are already widely accepted for the analysis of petroleum fuels[1]. Because the different petroleum fractions cover such a wide range of properties, more than one method is necessary to provide analysis for certain parameters. This is particularly true for liquefied petroleum gases which have a high volatility[2].

Compositional analysis of the heavier petroleum fractions (e.g., heating oils) becomes very complex. Methods for separation and identification of classes of compounds and individual components have been developed by EPA[3] and by the U. S. Bureau of Mines (American Petroleum Institute)[4]. A detailed discussion of these techniques which involve liquid chromatography separation and infra-red or gas chromatography/mass spectrometry identification techniques is beyond the scope of this study.

The ASTM Annual Book of Standards[5] contains many alternative analyses for some of the parameters listed; our choice has been made from those which appeared to offer the widest applicability.

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Parts 23, 24, and 25: Petroleum Products and Lubricants," American Society for Testing and Materials, Philadelphia, Pennsylvania.

2. "Liquefied Petroleum Gas, Specifications and Test Methods," Gas Processors Association, Publication No. 2140-75.

3. "IERL-RTP Procedures Manual: Level 1 - Environmental Assessment," EPA 600/2-76-160a, June, 1976.

4. Haine, W. E. and Thompson, C. J., "Separating and Charactizing High Boiling Distilates - The USBM-API Procedure," U. S. ERDA, LERC/RI-75/5, July, 1975.

5. "Annual Book of ASTM Standards (1974) - Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.

6. "Annual Book of ASTM Standards (1974) - Part 30: Standard Method of Test for Total Nitrogen in Organic Materials by Modified Kjeldahl Method," American Society for Testing and Materials, Philadelphia, Pennsylvania.

Table III-1

ANALYSES FOR LIQUID PETROLEUM FUELS

	PREFERRED METHODS					
PARAMETER	LIQUIFIED PETROLEUM GAS	GASOLINE	GAS TURBINE FUELS	DIESEL FUEL	HEATING OIL	WASTE LUBRICATING OILS
1. Carbon (Total) and Hydrogen	NA	ASTM D 3178	ASTM D 3178	ASTM D 3178	ASTM D 3178	ASTM D 3178
2. Nitrogen	NA	NA	ASTM E 258	ASTM E 258	ASTM E 258	ASTM E 258
3. Sulfur	ASTM D 2784	ASTM D 1266	ASTM D 129	ASTM D 129	ASTM D 129	ASTM D 129
4. Oxygen	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]
5. Chlorine	NA	NA	NA	NA	ASTM D 808	ASTM D 808
6. Water and Sediment	NA	ASTM D 1094	ASTM D 2709	ASTM D 2709	ASTM D 1796	ASTM D 1796
7. Ash	NA	NA	ASTM D 482	ASTM D 482	ASTM D 482	ASTM D 482
8. Calorific Value	NA	ASTM D 240	ASTM D 240	ASTM D 240	ASTM D 240	ASTM D 240
9. Carbon Residue	ASTM D 2158[b]	NA	ASTM D 524	ASTM D 524	ASTM D 524	ASTM D 524
10. Distillation	NA	ASTM D 86	ASTM D 86	ASTM D 86	ASTM D 86	ASTM D 86
11. Vapor Pressure	ASTM D 1267	ASTM D 323	ASTM D 323	NA	NA	NA
12. Flash Point	NA	ASTM D 93	ASTM D 93	ASTM D 93	ASTM D 93	ASTM D 93
13. Pour Point	NA	ASTM D 97	ASTM D 97	ASTM D 97	ASTM D 97	ASTM D 97
14. Viscosity	NA	NA	ASTM D 445	ASTM D 445	ASTM D 445/ ASTM D 88	ASTM D 445/ ASTM D 88
15. Density	ASTM D 1657	ASTM D 1298	ASTM D 1298	ASTM D 1298	ASTM D 1298	ASTM D 1298
16. Corrosion	ASTM D 1838	ASTM D 130	ASTM D 130	ASTM D 130	ASTM D 130	ASTM D 130

NA - Not Applicable

a. Obtained by difference.
b. Residue of higher boiling hydrocarbons, not carbon residue.

Table III-2

ANALYSES FOR LIQUID PETROLEUM FUELS

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (g)[e]	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Carbon (Total) and Hydrogen	ASTM D 3178	0.2	(30 - 70)	
2. Nitrogen	ASTM E 258	∿ 2	15 - 25	
3. Sulfur	ASTM D 2784	24 - 40		LF-1
	ASTM D 1266	2 - 15	20	LF-2
	ASTM D 129	0.6 - 1.0	25	LF-2
4. Oxygen	---	---	---	
5. Chlorine	ASTM D 808	0.8	20	
6. Water and Sediment	ASTM D 2709	100 ml	5	
	ASTM D 1796	50 - 60	6.5 - 20	
7. Ash	ASTM D 482	100		
8. Calorific Value	ASTM D 240	0.6 - 0.7	24 - 40	LF-5
9. Carbon Residue	ASTM D 2158	100 ml		
	ASTM D 524	50 ml	15	
10. Distillation	ASTM D 86	100 ml	25	
11. Vapor Pressure	ASTM D 1267	1,200 ml		
	ASTM D 323	1 - 7 liters	10 - 20	
12. Flash Point	ASTM D 93	75 - 90	16 - 25	
13. Pour Point	ASTM D 97	45 - 55	12 - 20	
14. Viscosity	ASTM D 445	---[f]	8 - 15	
	ASTM D 88	100 ml	13.5 - 25	
15. Density	ASTM D 1657	600 ml		
	ASTM D 1298	---[f]	5	
16. Corrosion	ASTM D 1838	30 - 90		
	ASTM D 130	30 - 90	6.5 - 20	

Notes appear on following page.

Notes to Table III-2:

a. All methods given are by the American Society for Testing and Materials. Specific references are cited in Table III-3 for each parameter.
b. These are the sample requirements for a single analysis.
c. Estimates based on prices charged by analytical services laboratories for petroleum fuels in early 1977.
d. See Appendix A for details.
e. Note that many values are in ml.
f. The amount needed varies with the type of equipment used and, for viscosity, with the value of the viscosity.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
1. Carbon (Total) and Hydrogen	ASTM D 3178	5	A weighed sample is burned in a closed system and the products of combustion fixed in an absorption train. CO_2 absorber may contain NaOH, KOH, or soda lime. Moisture absorber is anhydrous magnesium perchlorate ($Mg(ClO_4)_2$).	Method developed for coal and coke. Sample boats may have to be modified to hold liquid sample. Not applicable to LPG.	(P) Not specified for petroleum liquids. For coal and coke: **Repeatability:** Carbon - 0.3% Hyrdogen - 0.07%
2. Nitrogen	ASTM E 258 Modified Kjeldahl (See Note #1)	6	A sample is digested in a mixture of sulfuric acid, potassium sulfate and mercuric oxide converting nitrogen to ammonium sulfate. After mercury is precipitated with sodium sulfide, the solution is made alkaline with sodium hydroxide and the liberated ammonia distilled into an acid solution. The amount of acid neutralized is determined by titration with sodium hydroxide.	Method developed for nitrogen containing organic compounds. Not applicable for materials containing N-O, N-N linkages. Should be applicable for petroleum liquids, except LPG.	(P) Not specified for petroleum liquids, for organic compounds in general: Repeatability: 0.1% absolute for two results, each the average of duplicate determinations. See Reference #6 for additional information. Reproducibility: 0.2% absolute for two results, each the average of duplicate determinations. See Reference #6 for additional information.
3. Sulfur	A. ASTM D 129 General Bomb (See Note #2)	1	A sample is oxidized in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined gravimetrically as barium sulfate.	Generally applicable for petroleum products that are not highly volatile and that contain at least 0.1% sulfur. Not applicable to LPG, gasoline, or lubricating oils containing additives.	(P) Repeatability: 0.4% to 0.6% when S is between 0.1% and 1.0%. Reproducibility: 0.05% to 0.09% When S is between 0.1% and 1.0%. See Reference #1 for additional information.

All notes appear on the last page of this table.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
3. Sulfur continued	B. ASTM D 1266 Lamp Method	1	A sample is burned in a closed system using a suitable wick lamp with an atmosphere of 70% CO_2, 30% O_2. The oxides of sulfur are oxidized to sulfuric acid with hydrogen peroxide. Sulfate in the absorbant is determined by titration with NaOH or by precipitation as $BaSO_4$.	Applicable to volatile petroleum products that contain more than 0.002% sulfur and can be completely burned in a wick lamp.	(P) **Repeatability:** 5 ppm - 80 ppm: 0.116 × ppm S 80 ppm: (0.01 × ppm S) + 8.5 **Reproducibility:** 5 ppm - 125 ppm: 0.145 × ppm S 125 ppm - 280 ppm: (0.508 × ppm S) - 45.4
	C. ASTM D 2784 Oxy-hydrogen Burner	1	A sample is burned in an oxy-hydrogen burner in CO /O atmosphere. Oxides in sulfur are absorbed in hydrogen peroxide and oxidized to sulfuric acid. Sulfate ion is determined by titration with barium perchlorate or by precipitation of barium sulfate followed by trubidometry.	Applicable to LPG containing more than 1 ppm of sulfur, not more that 100 ppm halogen.	Not stated
	D. ASTM D 1552 High-Temperature Method	1	A sample is burned in a stream of oxygen at high temperature to convert about 97% of the sulfur to SO_2. The combustion products are absorbed in acid solution of KI/starch indicator. Potassium iodate is added as the combustion proceeds and the amount of standard iodate consumed is a measure of the sulfur content of the sample.	Applicable to petroleum fractions boiling above 350°F, particularly lubricating oils containing additives. Chlorine interferes above 1%, nitrogen may interfere above 0.1%.	(P) **Repeatability:** 0 - 0.5 wt. % S: 0.05 0.5 - 1.0 wt. % S: 0.07 1.0 - 2.0 wt. % S: 0.10 **Reproducibility:** 0 - 0.5 wt. % S: 0.08 0.5 - 1.0 wt. % S: 0.11 1.0 - 2.0 wt. % S: 0.17
4. Oxygen	ASTM D 271	5	Oxygen is determined indirectly by subtracting from 100 the percentages of hydrogen, carbon, sulfur, nitrogen, and ash.	Method developed for coal and coke.	Not known

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
5. Chlorine	ASTM D 808 Bomb Method (See Note #3)	1	Sample is oxidized by combustion in a bomb containing oxygen under pressure. The chlorrine compounds liberated are absorbed in a sodium carbonate solution and the amount of chlorine present determined gravimetrically by precipitation as silver chloride.	Method developed for lubricating oils and greases. Assumes other halogens are not present; lower limit of applicability is 0.1% chlorine.	(P) For lubricating oils and greases: Repeatability: 0.07 % for chlorine content in range of 0.1% to 2%. Reproducibility: 0.10% for chlorine content in range of 0.1% to 2%.
6. Water and Sediment	A. ASTM D 1796 Centrifuge (See Note #4)	1	The combined volume of water and sediment is measured volumetrically at the bottom of a centrifuge tube after a 50:50 solvent/sample mixture is centrifuged in a specified manner and at a specific temperature (49°C, or 60°C, if wax contributes to volume of water and sediment).	Applicable to crude oils and fuel oils (based on petroleum). Not applicable if water content is less than 0.05%.	(P) Repeatability: Ranges from 0.01% to 0.07% when value is 0.1% to 1.0%, respectively. Reproducibility: Ranges 0.11% to 0.20% when value is 0.1% and 1.0%, respectively.
	B. ASTM D 95 Water by Distillation	1	The sample is heated under reflex with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and measured volumetrically.	Applicable to crude petroleum, tars, and products derived from these materials.	(P) Repeatability: 0.1 ml if if water collected is < 1.0 ml. Reproducibility: 0.2 ml if water collected is < 1.0 ml.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
7. Ash	ASTM D 482 (See Note #3)	1	A sample is ignited in a crucible or evaporating dish and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled and weighed.	Applicable to most types of petroleum oils, including crude, residual fuels, distilates, and lubricating oils (containing no additives).	(P) Repeatability: 0.002% when ash is in range of 0.002% to 0.15%. Reproducibility: 0.004% when ash is in range of 0.002% to 0.15%. See Reference #1 for additional information.
8. Calorific Value	ASTM D 240 (See Notes #3 and #5)	1	A weighed sample is burned in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion. Allowance is made for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.	Applicable to a wide variety of substances, but particularly to liquid hydrocarbon fuels of both low and high volatility.	(P) Repeatability: 30.6 cal/g (55 Btu/lb) Reproducibility: 97.2 cal/g (175 But/lb)
9. Carbon Residue	A. ASTM D524 Rams-bottom (See Note #6)	1	A sample is placed in a special glass bulb having a capillary opening and then placed in a metal furnace maintained at ∿ 550°C. Heating is for 20 minutes. The bulb is then cooled in a dessicator and weighed. A modification is given for light distilate oils; the method, as given above, is used on a 10% distillation residue of the sample.	Applicable to relatively non-volatile petroleum products which partially decompose on distillation at atmospheric pressure. High ash content may give erroneously high values.	(P) Repeatability: 0.25% for average carbon residue of 0.1%. See Reference #1 for other points. Reproducibility: 0.035% for average carbon residue of 0.1%. See Reference #1 for other points.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
9. Carbon Residue continued	B. ASTM D 189 Conradson (See Note #6)	1	A sample is placed in a covered crucible and subjected to destructive distillation. At the end of a 30 minute heating period the crucible is cooled and weighed. Modifications are prescribed for high residue materials.	Applicable to relatively non-volatile petroleum products which partially decompose at atmospheric pressure. High ash content may give erroneously high values.	(P) Repeatability: 0.022% for average carbon residue of 0.0%. See Reference #1 for other points. Reproducibility: 0.058% for average carbon residue of 0.1%. See Reference #1 for other points.
	C. ASTM D2158 Residues (See Note #6)	1	A 100 ml sample of LPG is weathered in a 100 ml centrifuge tube. The volume of residue remaining at 100°F is measured.	Applicable to sample of LPG such as propane, butane, or mixtures. These residues are higher boiling hydrocarbons not carbon residue.	(P) Repeatability: Residue number 0 - 20: 5 20 - 40: 10 40 - 60: 20 Reproducibility: Residue number 0 - 20: 10 20 - 40: 10 40 - 60: 30
10. Distillation	ASTM D 86 Petroleum Products	1	A 100 ml sample is distilled under prescribed conditions which depend on the vapor pressure and initial and final distillation points. Systematic observations of temperature and condensate volume are made, and the reported results calculated from their data.	Applicable to motor and aviation gasolines, aviation turbine fuels, distilate fuel oils, and similar petroleum products.	(P) Varies with the initial boiling point and end point of the material and with the rate of change of thermometer readings. See Reference #1 for data.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S)** No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
11. Vapor Pressure	A. ASTM D 323 Reid Method	1	One chamber of the apparatus is filled with a chilled sample, and connected to an air chamber at 37.8°C (100°F) or other temperature. The apparatus is immersed in a constant-temperature bath at 37.8°C (100°F) and shaken until equilibrium is reached. The vapor pressure is then obtained from manometer readings, suitably corrected if the air chamber was not initially at 37.8°C (100°F).	Applicable to crude (petroleum) oil and volatile non-viscous petroleum products, except liquid petroleum gases.	(P) Repeatability: Varies with vapor pressure; is 0.2% pressures in range of .35 to 1.1 kg/cm^2 (5 to 16 lbs).
	B. ASTM D 1267 LPG Method	1	Similar to the Reid Method, the test apparatus consists of two interconnected chambers and is equipped with a pressure guage. It is purged with sample then completely filled. 40% is subsequently withdrawn to provide free space for product expansion. The apparatus is equilibrated at 100°F and the guage pressure observed.	Applicable to LPG containing less than 5% hydrocarbons boiling above 32°F and with vapor pressure not exceeding 225 psi.	(P) Repeatability: 0.5 lb + 0.5% of mean value. Reproducibility: 1.01 lb + 0.5% of mean value.
12. Flash Point	ASTM D 93 Pensky-Marteus Closed Cup	1	A sample is heated in a covered cup at a slow, constant rate with continual stirring. A small flame is directed into the cup-through opening in the cover - at regular intervals with simultaneous interruption of the stirring. The flash point is the lowest temperature at which the vapor above the sample is ignited by the test flame.	Applicable to fuel oils, lube oils, and other petroleum liquids.	(P) Repeatability: 2°C for flash points under 104.4°C, 5.5°C for flash. Reproducibility: 3.5°C for flash points under 104.4°C, 8.5°C for flash points above 104.4°C. See Reference #1 for additional data on precision for viscous materials.

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETERS	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
13. Pour Point	ASTM D 97		After preliminary heating, a sample is cooled at a specified rate and examined at intervals of 3°C (5°F) for flow characteristics. The lowest temperature at which movement of the oil is observed is the pour point. A modification for determining the lower (minimum) pour point of black oil, cylinder stock and non-distilate fuel oil is given.	Applicable to any petroleum oil.	(P) Repeatability: 3°C (5°F) Reproducibility: 6°C (10°F) - above not applicable when modified procedure is used.
14. Viscosity	A. ASTM D 445 Kinematic and Dynamic (See Note #7)	1	The time (in seconds) it takes a fixed volume of sample to flow through a capillary is measured. The capillary is calibrated and used with a reproducable driving head and with a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscosity is calculated from the kinematic viscosity. Test temperature must be specified by the parties concerned.	Applicable to liquid petroleum products. Not LPG.	(P) Repeatability: 0.35% of mean Reproducibility: 0.7% of mean
	B. ASTM D 88 Saybolt (See Notes #7 and #8)	1	The time required for a 60 ml sample to flow through a calibrated orifice is measured under carefully controlled conditions. This time is corrected by an orifice factor and reported as the viscosity of the sample at that temperature. Test temperature must be specified by the parties concerned.	Applicable to petroleum products at test temperatures between 21.1°C and and 98.9°C (70°F and 210°F).	Not given

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
15. Density	A. ASTM D 1298 Density, Specific Gravity, or API Gravity	1	A sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. An appropriate hydrometer is lowered into the sample and allowed to settle. The density is then read from the hydrometer scale where it breaks the liquid surface. Test temperature preferred near 15°C (60°F) but may be between (18°C and 90°C [0°F and 195°F). Test temperature should be specified by parties concerned. All readings are reduced to 15°C (60°F) for reporting.	Applicable to crude petroleum and petroleum products normally handled as liquids and having a Reid vapor pressure of 1.8 kg/cm^2 (26 lbs/in^2) or less.	(P) **Repeatability:** 0.0005 to 0.0006 for specific gravity and density, and 0.1 to 0.2 for API gravity, depending on type of oil. See Reference #1 for details. **Reproducability:** 0.0012 to 0.0015 for specific gravity and density, and 0.3 tp 0.5 for API gravity, depending on type of oil. See Reference #1 for details.
	B. ASTM D 1657 S.G. of light hydrocarbons by hydrometer	1	The pressurized cylinder is purged with the sample and then filled to a level at which the hydrometer floats freely. The density is read from the hydrometer scale where it breaks the liquid surface.	Applicable to LPG and other light hydrocarbons with Reid vapor pressure above 26 lb/in^2.	(P) **Repeatability:** 0.001 **Reproducibility:** 0.003
16. Corrosion	A. ASTM D 130 Copper Strip	1	A polished copper strip is immersed in a sample at a certain temperature for a time characteristic of the sample being tested. The copper strip is then removed, washed and compared with the ASTM Copper Strip Corrosion Standards Modifications are given for different types of petroleum products; in some cases the parties concerned must specify the temperature and time for the test.	Applicable to petroleum fuel oils, gasolines, lubricating oils, and certain other petroleum products.	Not given

Table III-3

METHODS OF ANALYSIS FOR LIQUID PETROLEUM FUELS

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
16. Corrosion continued	B. ASTM D 1838 Copper Strip LPG	1	This test is similar to ASTM D 130 above except that the container is a closed cylinder which can be pressurized. A temperature of 100°F for one hour is normally specified.	Applicable to LPG and similar low boiling petroleum liquids.	Not given

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*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference for duplicate results submitted by two or more laboratories. The original reference should be checked if precision is critical since the wording may imply special conditions for the applicability for the precision numbers given. Accuracy is given when listed in the original reference.

1. Data from analyses of two petroleum fuels for nitrogen by another method, ASTM 3228^{1}, are given in Appendix D. This is also a modified Kjeldahl method, but in only intended for use when nitrogen is present from 0.03 wt. % to 0.10 wt. %.

2. Data from analyses of two petroleum fuels for sulfur by another method, ASTM's "High Temperature Method" (ASTM D 1552)^{1} are given in Appendix D. A warning is given the nitrogen, when present in excess of 0.1%, may interfere with this method. Both shale oil and coal liquids. contain nitrogen above this level.

3. Data from analyses of two petroleum fuels by this method are given in Appendix D.

4. An essentially similar method is given in ASTM D96, "Standard Method of Test for Water and Sediment in Crude Oils"^{1}.

5. Another acceptable method is given in ASTM D 2382, "Standard Method of Test for Heat of Combustion of Hydrocarbon fuels by Bomb Calorimeter (High Precision Method)"^{1}. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.1%. The method can be used for a wide range of volatile and non-volatile materials where slightly greater differences in precision can be tolerated^{1}.

6. While no exact correlation exists between the Conradson (D 189) and Ramsbottom (D 524) methods for carbon residue, an approximate correlation for petroleum products has been found and is shown graphically in Reference #1. The correlation may not be valid for unusual petroleum products and ASTM urges caution in the application of this correlation at low carbon residues.

7. Tables are given in ASTM D 2161 for conversion of kinematic viscosity (in centistrokes) to Saybolt viscosity (in seconds) and the reverse.

8. This frequently used method was, until recently, included in Part 23 of ASTM's Book of Standards and was under the jurisdiction of ASTM Committee D-2 on petroleum products and lubricants. The method has recently transferred to the jurisdiction of ASTM Committee D-8 on asphalt and, accordingly, is now found in Part 15 of ASTM's Book of Standards. This transfer was in accordance with ASTM's plans to phase-out non-metric methods of test for petroleum products.

CHAPTER IV

SHALE OIL AND COAL LIQUIDS

1. INTRODUCTION/SUMMARY

A. Shale Oil

Shale oil is taken here to include any liquid organic material recovered from oil shale that is suitable for combustion. This includes both crude and refined shale oil. Shale oil is usually recovered from oil shale by a process called retorting, which subjects the shale to high temperatures (500°C to 550°C) at which the bonds linking the organic compounds to the remainder of the rock matrix are broken. The liberated compounds in the gaseous state are collected, condensed, and upgraded into a liquid product that is the rough equivalent of a crude oil. Other processes for the recovery of shale oil are being investigated, but are not as far advanced as retorting. While detailed development plans have been prepared for major shale oil production facilities, no shale oil is being commercially produced at this time (mid-1977).

Table IV-1 gives a summary listing of the fuel analyses that are important for shale oil (and coal liquids) combustion, along with an indentification of the preferred method of analysis and other information relating to the analyses. Additional information on the methods of analysis, including alternate methods for some parameters, is given in Section 3 of this chapter. All of the methods discussed are given by the American Society for Testing and Materials (ASTM), primarily in their standards for petroleum products and lubricants[1]. None of the methods discussed were developed specifically to include applicability to shale oils and coal liquids, but they are, nevertheless, expected to be adequate.

A set of standard methods for the analysis (specification testing) of shale oils and coal liquids do not exist, at present, though a laboratory method for the examination of crude shale oil was published by the Bureau of Mines in 1952[10]. The publication discusses several shale oil analyses including water, distillation, nitrogen, sulfur, specific gravity, pour point, and viscosity. The methods discussed are based on Bureau of Mines methods for petroleum[11] with modifications included to take into account the apparent poor heat stability of shale oil and the presence of large quantities of olefins and nitrogen compounds. Because the methods are not sufficiently detailed for use as a standard method, they have not been listed in this manual. Comments have, however, been included in Table IV-3 of this chapter, where appropriate.

Environmental assessments of processes using shale oil and coal liquids will need to include additional fuel analysis beyond those covered in this manual. Those likely to be required include trace elements in the fuel and in the ash, characterization of organic compounds present, and possibly, fuel-stability tests.

Shale oils differ from petroleum oils in composition and this may be an important aspect in an environmental assessment*. The organic material in oil shale is composed of a soluble bitumen fraction consisting of about 20% of the available organic matter, while the remainder exists as insoluble kerogen. The organic fraction of the shale may be around 15% of the oil shale. While oil shales are found in many areas of the U. S., the most important are found in the Green River formations in Colorado, Wyoming, and Utah. The kerogen of these shales consists of polycylic subunits interconnected by long chain alkanes and isoprenoids. The matrix also contains substantial amounts of entrapped, uncondensed alkanes, and fatty acids. The shale oil made from this material contains substantially higher amounts of nitrogen, oxygen, olefins, and ring compounds than does petroleum oil. Sulfur contents are generally lower than in petroleum oils. For some of the crude shale oils, over half of the material consists of compounds of sulfur, nitrogen, and oxygen, and less than half consists of pure hydrocarbons. The nitrogen compounds tend to concentrate in the higher boiling portions of shale oil.

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*Much of the information below is from Reference #2. Additional information is given in Reference #3.

Nitrogen in shale oil (naphtha fraction) is present as pyridines, pyrroles, and nitriles. Sulfur is primarily in the form of thiophenes, with some sulfides and small amounts of disulfides and thiols present. Oxygen compounds found include phenols and carboxylic acids. A majority of the nitrogen and sulfur compounds are heterocyclic - that is, with the heteroatoms contained in the rings. A significant amount of work has been done to determine the hydrocarbon types (including N- and S- compounds) in shale oils and procedures for shale oil characterization have been worked out. A bibliography, listing publications on this and other subjects, is given in Reference #4.

Of all the possible variables which affect the characteristics of shale oil, the method of production is, by far, the most significant. A variety of in situ and ex situ retorting processes have been proposed and each may lead to a different quality of oil. The composition of the shale oil will also vary from location to location and with the depth (of the original oil shale) at a given location.

B. Coal Liquids

The processing of coal to clean fuels - liquid, gaseous, or solid - is of considerable interest. There are two principal processes for accomplishing the conversion to liquid:

1. Pyrolysis - coal is heated to induce carbonization and thermal cracking.

2. Dissolution - coal is liquefied by an extractive process, usually through the agency of a solvent.

Both of these processes present a large number of alternative schemes for producing coal-derived liquids. For example, in dissolution of coal, processes might involve hydrogenation, catalysis, thermal liquefaction, and a host of other variables, singly or in combination.

The diversity of process conditions, as well as the many possible starting materials (including both coals and solvents), can lead to a multitude of product liquids. In addition, the final upgrading or refining of the coal liquid, e.g., to desulfurize, further increases the complexity of classifying the resulting oil. The precise chemical nature of most coal liquids is unknown. Frequently, the composition is described in terms of solubility in various solvents, such as hexane, pentane, pyridine, and benzene. Large fractions of coal liquids are often found to be asphatenes - a general term usually referring to high molecular weight compounds, boiling above 650°F and soluble in benzene (but insoluble in light parafins such as pentane)[12].

There are several apparent differences between petroleum products and coal liquids, such as[13]:

- The oils from coal contain large concentrations of oxygen and other heteroatoms.
- Branching of components is very different.
- High levels of polynuclear aromatics and rings substituted with one to three alkyl groups are present in the coal-derived materials.

The distinctions between the two types of oil are related to structure of the chemical compounds. Although the range of values for parameters will differ, the analytical procedures are essentially the same. Since separate methods for coal liquids have not, as yet, been proposed, those currently accepted for petroleum products are considered most appropriate. However, one must exercise caution in the analysis of coal liquids due to the possible inclusion of unreacted coal in the liquid. This problem is a result of the difficulty of solid/liquid separation in certain conversion processes.

2. SAMPLING

Procedures for collecting representative samples of shale oil or coal liquids will have to be tailored to (1) the nature of the material being sampled; (2) the nature of the fuel processing, handling, or storage equipment; and, (3) the precision and accuracy requirements of the analyses to be carried out. Since neither material is currently in commercial production, most sampling in the near term will be connected with bench or pilot scale research facilities.

Standard sampling methods for shale oil and coal liquids have not been developed, but the procedures given in ASTM D 270, "Standard Method of Sampling Petroleum and Petroleum Products"[1], will give a significant amount of guidance. This "method" actually includes numerous methods for sampling from a wide variety of containers for a wide variety of sample types, as shown by the examples below.

General Methods: bottle or grab, tap, continuous, dipper, tube, thief, boring, grab, and others;

Sample Containers: stationary tanks, ship or barge tanks, tank cars, and packaged lots (e.g., cans, drums, barrels);

Sample Types: average, all-levels, running, spot, top, upper, middle, lower, clearance, bottom, drain, water and sediment, composite, and several others.

The parties concerned should agree on a sampling procedure for each project. It should be noted that several ASTM methods of analysis require a specific sampling procedure to be used, including D 323 - Reid Vapor Pressure - which is included in this manual.

ASTM D 270 also covers specifications for sample containers, sample handling, labeling, and shipping. Because shale oil and coal liquids may contain carcinogens, laboratory coats and gloves should be work whenever there is the chance of spillage. The gloves should be made of butyl rubber, rather than neoprene or any other material, since they have been found to have the slowest permeation rate for a similar material, coal tar creosote[7].

3. ANALYSES

Table IV-2 gives, for each parameter of interest, additional information on the method(s) of analysis deemed suitable. When more than one method is listed, the preferred method is given first. The parameters are listed in the order given in Table IV-1.

It should be noted that none of the listed methods were developed for specific applicability to shale oil and coal liquids. Most methods were developed for petroleum and petroleum products. While it is expected that the listed methods will be generally applicable to shale oil and coal liquids, this has yet to be proven by laboratory tests. It is possible that unanticipated problems will require some methods modifications.

Caution should be used in the comparison of any precision inforamtion given in Table IV-2. Sample homogeneity may not be comparable and the absolute value of the parameters being measured may differ significantly in some cases.

Specific Comments on Shale Oil

Many crude shale oils contain a substantial quantity of water, often in the form of a stable emulsion. This water may be removed by distillation. The Bureau of Mines has recommended drying samples of crude shale oil, prior to subsequent analyses, with any equipment (e.g., drying oven, flask, tubing, condenser, and receiver) that provides for the removal of water from the sample without overheating or loss of oil[10]. The water content may be measured, by weight difference, by this method, but may not be as accurate as the method specified in this manual - ASTM D 95.

The Bureau of Mines report states that the specific gravity, sulfur content, nitrogen content, pour point, and viscosity are to be obtained on the dried sample. This may not always be desirable for combustion studies and the parties concerned should agree on the basis of the reporting.

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Parts 23, 24, and 25: Petroleum Products and Lubricants," American Society for Testing and Materials, Philadelphia, Pennsylvania.

2. "Report of the Conference-Workshop entitled Analytical Chemistry Pertaining to Oil Shale and Shale Oil," held June 24-25, 1974, at the National Science Foundation, Washington, D. C.

3. "Fuel Contaminants - Volume 1: Chemistry," U. S. Environmental Protection Agency, Office of Research and Development, Washington, D. C., 1976.

4. "A Bibliography of Oil Shale and Shale Oil," U. S. Energy Research and Development Administration, Laramie Energy Research Center, Laramie, Wyoming, 1974 - plus addendums for 1975 and 1976.

5. "Annual Book of ASTM Standard (1974) - Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.

6. "Annual Book of ASTM Methods (1974) - Part 30: Standard Method of Test for Total Nitrogen in Organic Materials by Modified Kjeldahl Method," American Society for Testing and Materials, Philadelphia, Pennsylvania.

7. Personal communication from Mr. Gerard C. Colletta, Arthur D. Little, Inc., April, 1977. Selection of butyl rubber is based on preliminary results of laboratory tests carried out by Arthur D. Little, Inc., for the National Institutes of Occupational Safety and Health in a program entitled, "Development of Performance Criteria for Protective Clothing Used Against Carcinogenic Liquids."

8. Lake, G. R., McCutchan, P., Van Meter, R., and Neel, J. C., "(Determination of Nitrogen in Shale Oil and Petroleum) Effects of Digestion Temperature on Kjeldahl Analysis," Analytical Chemistry, Volume 23, No. 11, pages 1634-1638 (1954).

9. Ball, J. S. and Van Meter, R., "Determination of Nitrogen in Shale Oil and Petroleum - Application of Established Methods," Analytical Chemistry, Volume 23, No. 11, pages 1632-1634 (1954).

10. Stevens, R. F., Dinneen, G. V., and Ball, J. S., "Analysis of Crude Shale Oil," U. S. Department of the Interior, Bureau of Mines Report of Investigations No. 4898, 1952.

11. Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L., "The Bureau of Mines Routine Method for the Analysis of Crude Petroleum: I - The Analytical Method," Bureau of Mines Bulletin 490, 1951.

12. Whitehurst, D. D., Farcasiu, M., and Mitchell, T. O., "The Nature and Origin of Asphaltenes in Processed Coals," Mobil Research and Development Corporation, Princeton, New Jersey.

13. Sharkey, A. G., Jr., "Mass Spectrometric Analysis of Process Streams for Coal-Derived Fuels," Energy Research and Development Administration, Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania.

Table IV-1

ANALYSES FOR SHALE OIL AND COAL LIQUIDS

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (g)	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Carbon (Total) and Hydrogen	ASTM D 3178	0.2	15 - 30	
2. Nitrogen	ASTM E 258	≲ 2.[e]	15 - 20	
3. Sulfur	ASTM D 129	0.6 - 1.0[e]	8 - 25	LF-2
4. Oxygen	ASTM D 271	NP	---	
5. Chlorine	ASTM D 808	0.8[e]	∿ 20	
6. Water and Sediment	ASTM D 1796	50. - 60.	5 - 15	
7. Ash	ASTM D 482	100.[e]	10 - 15	
8. Calorific Value	ASTM D 240	0.6 - 0.7[e]	10 - 30	LF-5
9. Carbon Residue	ASTM D 189	10.	10 - 15	
10. a. Distillation (distilates)	ASTM D 86	100. - 120.	10 - 30	
b. Distillation (crudes)	ASTM D 285	300 +	10 - 30	
11. Vapor Pressure	ASTM D 323	1. - 7. liters	15 - 20	
12. Flash Point	ASTM D 93	∿ 75. - 90.	7 - 15	
13. Pour Point	ASTM D 97	∿ 45. - 55.	7 - 20	
14. Viscosity	ASTM D 445	---[f]	7 - 20	
15. Density	ASTM D 1298	---[f]	4 - 10	
16. Corrosion	ASTM D 130	∿ 30. - 90.	6 - 20	

Notes on following page.

Notes for Table IV-1:

NP - Not Pertinent

a. All methods given are by the American Society for Testing and Materials. Specific references are cited in Table IV-2 for each parameter.
b. These are the sample requirements for a single analysis.
c. Estimates based on prices charged by analytical services laboratories for petroleum fuels in early-1977.
d. See Appendix A for details.
e. The amount needed varies with the value of the parameter being measured.
f. The amount needed varies with the type of equipment used and, for viscosity, with the value of the viscosity.

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
1. Carbon (Total) and Hydrogen	ASTM D 3178	5	A weighed sample is burned in a closed system and the products of combustion fixed in an absorption train. CO_2 absorber may contain NaOH, KOH, or soda lime. Moisture absorber is anhydrous magnesium perchlorate ($Mg(ClO_4)_2$).	Method developed for coal and coke. Sample boats may have to be modified to hold liquid samples.	(P) Unknown for SO and CL. For coal and coke: Repeatability: Carbon - 0.3% Hydrogen - 0.07%
2. Nitrogen	ASTM E 258 Modified Kjeldahl (See Note #1)	6	A sample is digested in a mixture of sulfuric acid, potassium sulfate and mercuric oxide converting nitrogen to ammonium sulfate. After mercury is precipitated with sodium sulfide, the solution is made alkaline with sodium hydroxide and the liberated ammonia distilled into an acid solution. The amount of acid neutralized is determined by titration with sodium hydroxide.	Method developed for nitrogen-containing organic compounds. Not applicable for materials containing N-O, N-N linkages. Should be applicable to SO and CL.	(P) Unknown for SO and CL. For organic compounds in general expect: Repeatability: 0.1% absolute for two results, each the average of duplicate determinations. See Reference #6 for additional information. Reproducibility: 0.2% absolute for two results, each the average of duplicate deterinations. See References #6 and #9 for additional information.
3. Sulfur	ASTM D 129 General Bomb (See Note #2)	1	A sample is oxidized in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined gravimetrially as barium sulfate.	Generally applicable to petroleum products that are not highly volatile and that contain at least 0.1% sulfur. Should be applicable to SO and CL.	(P) Unknown for SO and CL. For petroleum oils: Repeatability: 0.04% to 0.06% when S is between 0.1% and 1.0%. Reproducibility: 0.05% to 0.09% when S is between 0.1% and 1.0%. See Reference #1 for additional information.
4. Oxygen	ASTM D 271	5	Oxygen is determined indirectly by subtracting from 100 the percentages of hydrogen, carbon, sulfur, nitrogen, and ash.	Method developed for coal coke.	Not known

All notes appear on the last page of this table.

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
5. Chlorine	ASTM D 808 Bomb Method (See Note #3)	1	Sample is oxidized by combustion in a bomb containing oxygen under pressure. The chlorine compounds liberated are absorbed in a sodium carbonate solution and the amount of chlorine present determined gravimetrically by precipitation as silver chloride.	Method developed for lubricating oils and greases. Assumes other halogens are not present. Lower limit of applicability is 0.1% chlorine which may be higher than values found in most SO and CL.	(P) Unknown for SO and CL. For lubricating oils and greases: __Repeatability:__ 0.07% for chlorine content in range of 0.1% to 2% __Reproducibility:__ 0.10% for chlorine content in range of 0.1% to 2%.
6. Water and Sediment	A. ASTM D 1796 Centrifuge (See Note #4)	1	The combined volume of water and sediment is measured volumetrically at the bottom of a centrifuge tube after a 50:50 solvent/sample mixture is centrifuged in a specified manner and at a specific temperature (49°C, or 60°C if wax contributes to volume of water and sediment).	Applicable to crude oils and fuel oils (based on petroleum). Should be applicable to SO and CL. Not applicable if value is less than 0.05%.	(P) Unknown for SO and CL. For petroleum crude and fuel oils: __Repeatability:__ Ranges from 0.1% to 0.07% when value is 0.1% and 1.0%, respectively. __Reproducibility:__ Ranges from 0.11% to 0.20% when value is 0.1% and 1.0%, respectively,
	B. ASTM D 95 Water by Distillation	1	The sample is heated under reflux with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and measured volumetrically.	Applicable to crude petroleum, tars, and products derived from these materials. Should be applicable to SO and CL.	(P) Unknown for SO and CL. For petroleum oils: __Repeatibility:__ 0.1 ml if water collected is < 1.0 ml. __Reproducibility:__ 0.2 ml if water collected is < 1.0 ml.

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
6. Water and Sediment continued	C. ASTM D 473 Sediment by Extraction	1	A sample is placed in a refractory thimble and extracted with hot toluene until the residue reaches constant weight.	Applicable for crude petroleum and fuel oils. Should be applicable to SO and CL.	(P) Unknown for SO and CL. For petroleum oils with 0.0% to 0.4% sediment: **Repeatability:** 0.017 S % + 0.255 S % where S is average weight result in weight %. **Reproducibility:** 0.033 S% + 0.255 S % where S is the average result in weight %.
7. Ash	ASTM D 482 (See Note #3)	1	A sample is ignited in a crucible or evaporating dish and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled and weighed.	Applicable to most types of petroleum oils, including crude, residual fuels, distillates, and lubricating oils (containing no additives). Should be applicable to SO and CL.	(P) Unknown for SO and CL. For petroleum oils: **Repeatability:** 0.002% when ash is in range of 0.002% to 0.15%. **Reproducibility:** 0.004% when ash is in range of 0.002% to 0.15%. See Reference #1 for additional information.
8. Calorific Value	ASTM D 240 (See Notes #3 and #5)	1	A weighed sample is burned in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion. Allowance is made for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.	Applicable to a wide variety of substances, but particularly to liquid hydrocarbon fuels of both low and high volatility. Should be applicable to SO and CL.	(P) Unknown for SO and CL. For others: **Repeatability:** 30.6 cal/g (55 Btu/lb.) **Reproducibility:** 97.2 cal/g (175 Btu/lb.)

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

	SUGGESTED METHOD(S)				
PARAMETER	No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
9. Carbon Residue	A. ASTM D 189 Conradson (See Note #6)	1	A sample is placed in a covered crucible and subjected to destructive distillation. At the end of a 30 minute heating period, the crucible is cooled and weighed. Modifications are prescribed for high residue materials.	Generally applicable to nonvolatile petroleum products which particularly decompose at atmospheric pressure. High ash content may give erroneously high values. Should be applicable for crude SO and CL.	(P) Unknown for SO and CL. For other: Repeatability: 0.022% for average carbon residue of 0.1%. See Reference #1 for other points. Reproducibility: 0.058% for average carbon residue of 0.1%. See Reference #1 for other points.
	B. ASTM D 524 Ramsbottom (See Note #6)	1	A sample is placed in a special glass bulb having a capillary opening and then placed in a metal furnace maintained at ∿ 550°C. Heating is for 20 minutes. The bulb is then cooled in a dessicator and weighed. A modification is given for light distilate oils; the method, as given above, is used on a 10% distillation residue of the sample.	Generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure. High ash content may give erroneously high values. Method should be applicable for SO and Cl.	(P) Unknown for SO and CL. For others: Repeatability: 0.025% for average carbon residue of 0.1%. See Reference #1 for other points. Reproducibility: 0.035% for average carbon residue of 0.1%. See Reference #1 for other points.
10. Distillation	A. ASTM D 86 Petroleum Products	1	A 100-ml sample is distilled under prescribed conditions which depend on the vapor pressure and initial and final distillation points. Systematic observations of temperature and condensate volume are made, and the reported results calculated from these data.	Applicable to motor and aviation gasolines, aviation turbine fuels, distilate fuel oils, and similar petroleum products. Should be applicable for low boiling or distilate SO and CL.	(P) Varies with the initial boiling point and end point of the material and with the rate of change of thermometer readings. See Reference #1 for data.

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

PARAMETER	SUGGESTED METHOD(S		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
10. Distillation continued	B. ASTM D 285	1	One or more 300-ml portions are distilled from a flask equipped with a fractionating column at a rate of 4 ml to 5 ml per minute to a predetermined thermometer reading. A 100-ml portion of the total distilate is distilled in accordance with ASTM D 86. The predetermined temperature for the initial crude distillation is specified by the parties concerned in the evaluation; it is not specified in the method.	Applicable for any crude petroleum of the class known commercially as refinable crude oils. Should be applicable for crude SO and CL.	Not given
11. Vapor Pressure	ASTM D 323 Reid Method	1	One chamber of the apparatus is filled with a chilled sample, and connected to an air chamber at 37.8°C (100°F) or other temperature. The apparatus is immersed in a constant-temperature bath at 37.8°C (100°F) and shaken until equilibrium is reached. The vapor pressure is then obtained from manometer readings, suitably corrected if the air chamber was not initially at 37.8°C (100°F).	Applicable to crude (petroleum) oil and volatile non-viscous petroleum products, except liquified petroleum gases. Should be applicable for SO and CL.	(P) Unknown for SO and CL. For petroleum products: Repeatability: Varies with vapor pressure; is 0.2% for pressures in range of .35 kg/cm^2 to 1.1 kg/cm^2 (5 lbs to 6 lbs).
12. Flash Point	A. ASTM D 93 Pensky-Martens Closed Cup	1	A sample is heated, in a covered cup, at a slow, constant rate with continual stirring. A small flame is directed into the cup-through opening in the cover - at regular intervals with simultaneous interruption of the stirring. The flash point is the lowest temperature at which the vapor above the sample is ignited by the test flame.	Applicable for fuel oils, lube oils, and other liquids. Should be applicable for SO and CL.	(P) Unknown for SO and CL. For others (excluding suspensions): Repeatability: 2°C for flash points under 104.4°C. 5.5°C for flash points above 104.4°C. Reproducibility: 3.5°C for flash points under 104.4°C. 8.5°C for flash points above 104.4°C. See Reference #1 for additional information.

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
12. Flash Point continued	B. ASTM D 92 Cleveland Open Cup	1	A sample is placed in an open cup and its temperature increased rapidly at first and then at a slow, constant rate as the flash point is approached. At specified intervals, a test flame is passed across the cup. The lowest temperature at which the vapors ignite is the flash point.	Applicable to all petroleum products, except fuel oils and those having an open cup flash point below 79°C. Should be applicable for SO and CL.	(P) Unknown for SO and CL. For others: __Repeatability:__ 8°C __Reproducibility:__ 17°C
13. Pour Point	ASTM D 97		After preliminary heating, a sample is cooled at a specified rate and examined at intervals of 3°C (5°F) for flow characteristics. The lowest temperature at which movement of the oil is observed is the pour point. A modification for determining the lower (minimum) pour point of black oil, cylinder stock, and non-distilate fuel oil is given.	Applicable to any petroleum oil. Should be applicable for SO and CL.	(P) Unknown for SO and CL. For others: __Repeatability:__ 3°C (5°F) __Reproducibility:__ 6°C (10°F) (Above not applicable when modified procedure is used.)
14. Viscosity	A. ASTM D 445 Kinematic and Dynamic (See Note #7)	1	The time (in seconds) it takes a fixed volume of sample to flow through a capillary is measured. The capillary is calibrated and used with a reproducible driving head and with a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. The dynamic viscosity is calculated from the kinematic viscosity. Test temperature must be specified by the parties concerned.	Generally applicable to liquid petroleum products. Should be applicable for SO and CL.	(P) Unknown for SO and CL. For others: __Repeatability:__ 0.35% of mean __Reproducibility:__ 0.7% of mean

Table IV-2

METHODS OF ANALYSIS FOR SHALE OIL (SO) AND COAL LIQUIDS (CL)

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
14. Viscosity continued	B. ASTM D 88 Saybolt (See Notes #7 and #8)	1	The time required for a 60-ml sample to flow through a calibrated orifice is measured under carefully controlled conditions. This time is corrected by an orifice factor and reported as the viscosity of the sample at that temperature. Test temperature must be specified by the parties concerned.	Generally applicable to petroleum products at test temperatures between 21.1°C and 98.9°C (70°F and 210°F). Should be applicable for SO and CL.	Not given
15. Density	ASTM D 1298 Density, Specific Gravity, or API Gravity	1	A sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. An appropraite hydrometer is lowered into the sample and allowed to settle. The density is then read from the hydrometer scale where it breaks the liquid surface. Test temperature preferred near 15°C (60°F), but may be between -18°C and 90°C (0°F and 195°F). Test temperature should be specified by parties concerned. All readings are reduced to 15°C (60°F) for reporting.	Generally applicable to crude petroleum and petroleum products normally handled as liquids and having a Reid vapor pressure of 1.8 kg/cm^2 (26 lbs/in^2) or less. Should be applicable for SO and CL	(P) Unknown for SO and CL. For others: **Repeatability:** 0.0005 to 0.0006 for specific gravity and density, and 0.1 to 0.2 for API gravity, depending on type of oil. See Reference #1 for details. **Reproducibility:** 0.0012 to 0.0015 for specific gravity and density, and 0.3 to 0.5 for API gravity, depending on type of oil. See Reference #1 for details.
16. Corrosion	ASTM D 130 Copper Strip	1	A polished copper strip is immersed in a sample at a certain temperature for a time characteristic of the sample being tested. The copper strip is then removed, washed, and compared with the ASTM Copper strip Corrosion Standards. Modifications are given for different types of petroleum products; in some cases, the parties concerned must specify the temperature and time for the test.	Generally applicable to petroleum fuel oils, gasolines, lubricating oils, and certain other petroleum products. Should be applicable for SO and CL. The temperature and time best suited for SO and CL corrosion tests are unknown and should be determined by the parties concerned.	Not given

Notes for Table IV-2:

*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference for duplicate results submitted by two or more laboratories. The original reference should be checked if precision is critical since the wording may imply special conditions for the applicability of the precision numbers given. Accuracy is given when listed in the original reference.

1. Data from analyses of shale oil and coal liquids for nitrogen by another method, ASTM 3228[1], are given in Appendix D. This is also a modified Kjeldahl method, but is only intended for use when nitrogen is present from 0.03 wt. % to 0.10 wt. %.

2. Data from analyses of shale oil and coal liquids for sulfur by another method, ASTM's "High Temperature Method" (ASTM D 1552)[1], are given in Appendix D. A warning is given that nitrogen, when present in excess of 0.1%, may interfere with this method. Both shale oil and coal liquids contain nitrogen above this level.

3. Data from analyses of shale oil and coal liquids by this method are given in Appendix D.

4. An essentially similar method is given in ASTM D 96, "Standard Method of Test for Water and Sediment in Crude Oils"[1].

5. Another acceptable method is given in ASTM D 2382, "Standard Method of Test for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High Precision Method)"[1]. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.1%. The method can be used for a wide range of volatile and non-volatile materials where slightly greater differences in precision can be tolerated[1].

6. While no exact correlation exists between the Conradson (D 189) and Ramsbottom (D 524) methods for carbon residue, an approximate correlation for petroleum products has been found and is shown graphically in Reference #1. The correlation may not be valid for unusual petroleum products (and, thus, SO and CL), and ASTM urges caution in the application of this correlation at low carbon residues.

7. Tables are given in ASTM D 2161 for conversion of kinematic viscosity (in centistokes) to Saybolt viscosity (in seconds) and the reverse.

8. This frequently used method was, until recently, included in Part 23 of ASTM's Book of Standards and was under the jurisdiction of ASTM Committee D-2 on petroleum products and lubricants. The method has recently transferred to the jurisdication of ASTM Committee D-8 on asphalt and, accordingly, is now found in Part 15 of ASTM's Book of Standards. This transfer was in accordance with ASTM's plans to phase-out non-metric methods of test for petroleum products.

CHAPTER V

METHYL FUEL

1. INTRODUCTION/SUMMARY

Methyl fuel is taken here to include material produced in a methanol-synthesis type of operation where the higher alcohol impurities are not removed, but most of the water is removed. The fuel composition will vary depending on the feed stock used and the process involved, but, typically, it will be around 90% to 95% methanol, 0.1% to 10% higher alcohols, and 0.5% to 5% water.

Proposed raw materials for methyl fuel include: (1) middle-east flare gas (converted to methyl fuel at the well site); (2) domestic coal; and, (3) wastes, both domestic and agricultural. At present, methyl fuel is not being made commercially. Possible uses for the methyl fuel include: use as a fuel for boilers and gas turbines; use as a fuel - complete or as an additive to gasoline - for automobiles; or, regasification to Synthetic Natural Gas (SNG).

Table IV-1 gives a summary of the fuel analyses that are important for methyl fuel, along with an identification of the preferred method of analysis and other information relating to the analyses. Additional information on the methods of analyses, including alternate methods for some parameters, is given in Section 3 of this chapter. All of the methods discussed, except those for chloride and higher alcohols, are given by the American Society for Testing and Materials (ASTM). Many of these ASTM methods are specified as standard methods of analysis to be used for methanol. They have been identified in Table IV-1. The chloride and higher alcohol analyses prescribed are given by the Association of Official Analytical Chemists (AOAC).

No analyses for carbon, hydrogen, and oxygen have been prescribed, as their concentration may be calculated with sufficient accuracy one the concentrations of methanol, water, and higher alcohols are known. The methanol content may be derived from the specific gravity, viscosity, boiling point, or vapor pressure, if the content of higher alcohols is small. All of these properties vary with water content, and tables of values (at different water contents) are available in the literature[6] or in the manufacturer's data sheets. When the content of higher alcohols is large, the methanol content may be roughly estimated by subtracting the percentages of higher alcohols plus water from 100.

An analysis for sulfur has been included, even though the concentration is expected to be quite low. The catalysts used in making methyl fuel are quite sensitive to contamination by sulfur, and its concentration is accordingly reduced to low levels, often 0.1 ppm, in the feed material. Nitrogen will be present only to the extent that it is present in the feed material. Nitrogen compounds are likely to be present as amines in methyl fuel. Chlorides are likely to be present when methyl fuel is shipped by ocean-going tankers. Salt water contamination in the tanks is the source of the chlorides. The higher alcohols found in methyl fuel consist primarily of ethanol, n-propanol, and iso-butanol. They are desirable components of methyl fuel in one respect as they will increase the calorific value. Small amounts of other organics, such as methyl ether, acetone, and resins, may also be present. It is not clear, at this time, if certain additives would have to be added to methyl fuel to make it suitable for various uses and/or unsuitable for other uses.

If methyl fuel was to be investigated as a automotive fuel, then certain other analyses may need to be included. This may include, for example, research octane number, motor octane number, and corrosion tests other than the copper strip method.

2. SAMPLING

Procedures for collecting representative samples of methyl fuel will have to be tailored to (1) the nature of the material being samples; (2) the nature of the fuel processing, handling, or storage equipment; and, (3) the precision and accuracy requirements of the analyses to be carried out. Since methyl fuel is not currently in commercial production, most sampling in the near term will be connected with bench, or pilot, scale research facilities.

Methods for sample collection may be taken either from ASTM E 300, "Standard Recommended Practice for Sampling Industrial Chemicals"[5], or ASTM D 270, "Standard Method of Sampling Petroleum and Petroleum Products"[2]. The ASTM E 300 methods are specified in ASTM D 1152[5] for the collection of a representative sample of methyl alcohol. Method ASTM E 300 covers statistical considerations. The sample collection methods are based on those given in D 270, so the differences are minimal. Both methods include variations for sampling from a wide variety of containers for a wide variety of sample types, as shown by the examples below.

General Methods: bottle or grab, tap, continuous, dipper, tube, thief, boring, grab, and others;

Sample Containers: stationary tanks, ship or barge tanks, tank cars, and packaged lots (e.g., cans, drums, barrels);

Sample Types: average, all-levels, running, spot, top, upper, middle, lower, clearance, bottom, drain, water and sediment, composite, and several others.

The parties concerned should agree on a sampling procedure for each project.

3. ANALYSES

Table V-2 gives, for each parameter of interest, additional information on the methods of analysis deemed suitable. When more than one method is listed, the preferred method is given first. The parameters are listed in the order given in Table V-1.

It should be noted that none of the listed methods were developed for specific applicability to methyl fuel, though some are specifically applicable to methanol. While it is expected that the listed methods will be generally applicable to methyl fuel, this has yet to be proven by laboratory tests. It is possible that unanticipated problems will require some methods modifications.

Caution should be used in the comparison of any precision information given in Table V-2. Sample homogeneity may not be comparable and the absolute value of the parameters being measured may differ significantly in some cases.

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Part 30: Soap, Engine Coolants; Polishes; Halogenated Organic Solvents; Activated Carbon, Industrial Chemicals," American Society for Testing and Materials, Philadelphia, Pennsylvania.

2. "Annual Book of ASTM Standards (1974) - Part 23: Petroleum and Petroleum Products," American Society for Testing and Materials, Philadelphia, Pennsylvania.

3. "Annual Book of ASTM Standards (1974) - Part 31: Water," American Society for Testing and Materials, Philadelphia, Pennsylvania.

4. "Official Methods of Analysis of the Association of Official Analytical Chemist," William Horwitz (ed.), Twelfth Edition, 1975. Published by the Association of Official Analytical Chemists (AOAC), Washington, D. C.

5. "Annual Book of ASTM Standards (1974) - Part 29: Paint - Fatty Oils and Acids, Solvents, Miscellaneous; Aromatic Hydrocarbons; Naval Stores," American Society for Testing and Materials, Philadelphia, Pennsylvania.

6. See, for example, article by C. Carr and J.A. Riddick, "Physical Properties of Methanol-Water Systems," Ind. Eng. Chem, 43, 692-696, 1951.

Table V-1

ANALYSES OF METHYL FUEL

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (g)	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Nitrogen	ASTM E 258	2.	15 - 20	
2. Sulfur	ASTM D 1266 and ASTM D 516	20 10-50	∿ 20 ∿ 10	LF-2
3. Chloride	AOAC	100	∿ 15	
4. Water	ASTM E 346/E 203[e]	1-10	∿ 15	
5. Higher Alcohols	AOAC	100	30 - 50	
6. Nonvolatile Matter	ASTM D 1353[f]	100	∿ 10	
7. Calorific Value	ASTM D 240	1	10 - 30	
8. Specific Gravity	ASTM E346/D 891[e] (Method C)	25	4 - 10	
9. Viscosity	ASTM D 445	--[g]	7 - 20	
10. Distillation	ASTM D 1078[e,f]	100	10 - 20	
11. Flash Point	ASTM D 93	80	7 - 15	
12. Vapor Pressure	ASTM D 323	1-7 liters	15 - 20	
13. Corrosion Rate	ASTM D 1616	10	6 - 20	
14. Acidity	ASTM D 1613[e,f]	60	7 - 15	

All notes appear on the following page.

Notes for Table VI-1:

a. Specific references to methods listed are given in Table V-2. All method numbers beginning with 'D' or 'E' are from ASTM. AOAC refers to methods given by the Association of Official Analytical Chemists.
b. These are the approximate sample requirements for a single analysis of a material for which the method is directly applicable. Somewhat different amounts may be required for methyl fuel. The amounts required by a laboratory may be larger for a variety of reasons, including those connected with sample preparation.
c. Estimates based on prices charged by analytical service laboratories for petroleum products or water in early-1977.
d. See Appendix A for details.
e. These test methods are specified by ASTM for methanol in E 346, "Standard Methods for Analysis of Methanol"[5].
f. These test methods are specified by ASTM for methyl alcohol in D 1125, "Standard Specification for Methyl Alcohol"[5].
g. The amount needed varies with the type of equipment used and the viscosity of the sample.

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

PARAMETER	SUGGESTED METHOD(S) No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
1. Nitrogen	ASTM E 258 Modified Kjeldahl	1	A sample is digested in a mixture of sulfuric acid, potassium sulfate, and mercuric oxide converting nitrogen to ammonium sulfate. After mercury is precipitated with sodium sulfide, the solution is made alkaline with sodium hydroxide and the liberated ammonia distilled into an acid solution. The amount of acid neutralized is determined by titration with sodium hydroxide.	Method developed for nitrogen containing organic compounds. Not applicable for materials containing N-O, N-N linkages. May be applicable to MF.	(P) Unknown for MF. For organic compounds in general expect: Repeatability: 0.1% absolute for two results, each the average of duplicate determinations. See Reference #1 for additional information. Reproducibility: 0.2% absolute for two results, each the average of duplicate determinations. See Reference #1 for additional information.
2. Sulfur	A. ASTM D 1266 Lamp Method	2	A sample is burned in a closed system using a lamp and an artificial atmosphere (70% CO_2, 30% O_2). Sulfur oxides are adsorbed and oxidized to sulfuric acid with H_2O_2, and solution flushed with air to remove CO_2. Sulfur, as sulfate, in the adsorbent is determined acidimetrically by titration, or gravimetrically, by precipitation as $BaSO_4$.	Applicable to light petroleum products with sulfur contents above 0.002 wt %. Modification of procedure (Appendix A1 of Method) allows detection of 5 ppm sulfur. May be applicable to MF if sulfur is primarily connected with volatile compounds.	(P) Unknown for MF. For others with 0.01% to 0.04% sulfur: Repeatability: 0.005% Reproducibility: 0.010 + 0.025 S where S = total wt % sulfur in the sample.
	B. ASTM D 516 Sulfate in Water	3	Sulfate ion may be either (a) precipitated and weighed as $BaSO_4$ after removal of silica and other insoluble matter, (b) converted to $BaSO_4$ in a controlled manner and the turbidity measured, or (c) titrated in an alcoholic solution under acid conditions with $BaCl_2$ solution.	Applicable to water and wastewater. First method (a) directly applicable for samples containing ∿ 20 ppm sulfate ion; others are particularly useful below 20 ppm. May be applicable to MF if sulfur is primarily in form of sulfate ions.	(P) Unknown for MF. For other applicable samples: Method a: 1.0% Method b: 5% or 2 mg/l, whichever is greater. Method c: 0.7 mg/l for samples up to 100 mg/l. See Reference #3 for additional information.

All notes appear on the last page of this table.

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
3. Chloride	AOAC 9.043-9.045 Chloride (10)	4	Sample is titrated in an acid medium with $AgNO_3$ solution. End point is determined with pH meter and specified glass electrodes. Equivalence voltage predetermined with standard solution of chloride in ethanol.	Method developed for distilled liquors (spirits). Should be applicable to MF.	Not given
4. Water	ASTM E 346/E203 Karl Fisher Reagent	1	A sample is dissolved in a suitable liquid and titrated with Karl Fisher reagent, which is a mixture of iodine, sulfur dioxide, pyridine, and methanol or glycol ether. End point may be determined either visually or electrometrically.	Applicable for determination of free water and water of hydration in liquid organic compounds (plus other types of compounds) over a wide concentration range. Specifically applicable to determination of water in the presence of alcohols. Method specified by ASTM for testing of methanol.	(P) Unknown for MF. For others, varies with several factors; see Reference #1 for discussion. Sensitivity is ∿ 0.1 mg water for visual titrations; less than 0.02 mg for electrometric titrations.
5. Higher Alcohols	AOAC 9.075-9.080 Gas Chromatographic Method (16) and Alternative Method (17)	4	Quantitative determination of higher alcohols made by measurement of peak height after passing sample through gas chromatograph having a flame ionization detector. Column for Method 16 is 23% Carbowax 1500 on Chromosorb W; column for Method 17 is 2% glycerol and 2% 1,2,6-hexanetriol on Gas-Chrom R.	Method developed for distilled liquors (spirits), specifically to look for n-propyl alcohol, isobutyl alcohol, isoamyl alcohol and ethyl acetate in spirits. May be applicable to MF.	Not given

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
6. Nonvolatile Matter	ASTM D 1353	5	A sample is evaporated to dryness in a platinum evaporating dish over a steam bath. After further drying for ∿ 1 hour in an oven at 105°C, the nonvolatile matter is determined from the wieght of the residue in the dish.	Applicable to volatile solvents used in paint, varnish, lacquer and related products. Method specified by ASTM for testing of methyl alcohol.	(P) Unknown for MF. For others: Repeatability: 0.0009 g/100 ml for two results, each the average of duplicate determinations. Reproducibility: 0.0024 g/100 ml for two results, each the average of duplicate determinations.
7. Calorific Value	ASTM D 240	2	A weighed sample is burned in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations taken before, during, and after combustion. Allowance is made for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.	Applicable to a wide variety of substances, but particularly to liquid hydrocarbon fuels of both low and high volatility. Should be applicable to MF.	(P) Unknown for MF. For others: Repeatability: 30.6 cal/g (55 Btu/lb.) Reproducibility: 97.2 cal/g (175 Btu/lb.)
8. Specific Gravity	ASTM E 346/D 891 (Method C) Pycnometer	5	A calibrated pycnometer is filled with the sample and put in a water bath at 20°C for at least 30 minutes. At the end of this period, the liquid level in the pycometer is adjusted to the calibration mark, removed from the bath and weighed. The specific gravity is calculated as the ratio of the sample weight to an equal volume of water at 20°C.	Generally applicable to industrial aromatic hydrocarbons and related materials. Method specified by ASTM for testing of methanol.	(P) Unknown for MF. For methanol: Repeatability: 0.00008 units for difference in two values Reproducibility: 0.00055 units for difference in two values

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
9. Viscosity	ASTM D 445 Kinematic and Dynamic	2	The time (in seconds) it takes a fixed volume of sample to flow through a capillary is measured. The capillary is calibrated and used with a reproducible driving head and with a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. The dynamic viscosity is calculated from the kinematic viscosity. Test temperature must be specified by the parties concerned.	Generally applicable to liquid petroleum products. Should be applicable to MF.	(P) Unknown for MF. For others: Repeatability: 0.35% of mean Reproducibility: 0.7% of mean
10. Distillation	ASTM D 1078	5	A sample is distilled under conditions equivalent to a simple batch differential distillation. Distillation is at a rate of 4 to 5 ml/minute. Readings of the distillation thermometer are recorded after collecting 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 ml of distillate. Distillation is continued to the dry point and the temperature recorded.	Generally applicable to organic liquids boiling between 30°C and 300°C. Specifically applicable to oxygenated compounds (e.g., alcohols). Method specified by ASTM for testing of methanol.	(P) Unknown for MF. For acetone: Repeatability: Ranges from 0.09°C to 0.24°C from initial boiling to dry point. 0.26°C for distillation range. Reproducibility: Ranges from 0.32°C to 0.51 °C at various points. It is 0.66°C for distillation range. See Reference #5 for additional data.

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
11. Flash Point	A. ASTM D 93 Pensky-Martens Closed Cup	2	A sample is heated, in a covered cup, at a slow, constant rate with continual stirring. A small flame is directed into the cup - through an opening in the cover - at regular intervals with simultaneous interruprion of the stirring. The flash point is the lowest temperature at which the vapor above the sample is ignited by the test flame.	Applicable to fuel oils, lube oils, and other liquids. Should be applicable to MF.	(P) Unknown for MF. For others (excluding suspensions): **Repeatability:** 2°C for flash points under 104.4°C. 5.5°C for flash points above 104.4°C. **Reproducibility:** 3.5°C for flash points under 104.4°C. 8.5°C for flash points above 104.4°C. See Reference #2 for additional data on precision for viscous materials.
	B. ASTM D 92 Cleveland Open Cup	2	A sample is placed an in open cup and its temperature increased rapidly, at first, and then at a slow, constant rate as the flash point is approached. At specified intervals, a test flame is passed over the cup. The lowest temperature at which the vapors ignite is the flash point.	Applicable to all petroleum products except fuel oils and those having an open cup flash point below 79°C. Should be applicable to MF.	(P) Unknown for MF. For others: **Repeatability:** 8°C **Reproducibility:** 17°C
12. Vapor Pressure	ASTM D 323 Reid Method	2	A chamber of the apparatus is filled with a chilled sample and connected to an air chamber at 37.8°C (100°F) or other temperature. The apparatus is immersed in a constant temperature bath at 37.8°C 100°F) and shaken until equilibrium is reached. The vapor pressure is then obtained from manometer readings, suitably corrected if the air chamber was not initially at 37.8°C (100°F).	Applicable to crude (petroleum)oil and volatile non-viscous petroleum gases. Should be applicable to MF.	(P) Unknown for MF. For petroleum products: **Repeatability:** Varies with vapor pressure; is 0.2% for pressures in range of .35 to 1.1 kg/cm^2 (5 to 6 lbs.)

Table V-2

METHODS OF ANALYSIS FOR METHYL FUEL

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	No./Title	Ref.			
13. Corrosion	ASTM D 1616 Copper Strip	5	A polished copper strip is immersed in a test tube filled with the sample and heated at reflux temperature for 30 minutes. At the end of this period, the copper strip is removed, washed, and compared with copper strip corrosion standards.	Generally applicable to mineral spirits and certain other products used in the paint industry. Should be applicable to MF.	Not given
14. Acidity	ASTM D 1613	5	The sample is mixed with either an equal volume of water or an equal volume of alcohol, and titrated with aqueous sodium hydroxide solution to the phenolphthalein and end point. Acidity is reported as acetic acid.	Generally applicable to organic compounds and hydrocarbon mixtures used in paint, varnish, and lacquer solvents and diluents where acidity as acetic acid is below 0.05%. Method specified by ASTM for testing of methanol.	(P) Unknown for MF. For others: Repeatability: 0.0008% absolute for two results each the average of duplicate determinations. Reproducibility: 0.0014% absolute for two results each the average of duplicate determinations

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*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference for duplicate results submitted by two or more laboratories. The original reference should be checked if precision is critical, since the wording may imply special conditions for the applicability of the precision numbers given. Accuracy is given when listed in the original reference.

CHAPTER VI

COAL AND COKE

1. INTRODUCTION/SUMMARY

A. Coal

Coal is the term applied to those rocks in the earth's crust which are fossilized plants from prehistoric times. Coals are comprised of five major elements: carbon, hydrogen, oxygen, nitrogen, and sulfur. The material is non-homogeneous with respect to physical and chemical characteristics, and typically consists of alternating bands of bright and dull material. Classification by rank, according to ASTM D 388, divides coal into four major classes with regard to rank or age - anthracitic, bituminous, subbituminous, and lignitic. These classes are further broken down into sub-groups based on the limits of fixed carbon, volatile matter, and calorific value.

With two exceptions, the methods of analysis discussed herein, may be placed into two categories: proximate analysis and ultimate analysis. A proximate analysis includes moisture, volatile matter, ash, and fixed carbon (determined by difference) for a coal sample. An ultimate analysis includes moisture, carbon, hydrogen, nitrogen, sulfur, ash, and oxygen (by difference). Several components are common to both sets of analyses reducing the total number of determinations necessary to completely identify a particular coal sample. The two exceptions to proximate and ultimate analyses are chlorine content and the coal heating value which are important in evaluating the properties of a sample.

Table VI-1 presents a summary of the analyses for coal with the preferred methods. Section 3 of this chapter provides additional information on analytical procedures, as well as alternate methods. The preferred methods have all been selected from the American Society for Testing and Materials (ASTM) methods for coal and coke[1]. These procedures are approved by the American National Standards Institute and are generally accepted throughout the United States. They are essentially the same as those methods recommended by the Bureau of Mines for analyzing coal and coke[2] and the procedures accepted by the American Society of Mechanical Engineers in the Power Test Codes for Solid Fuels[3].

B. Coke

The principal use of coke in the United States is as a fuel in the iron blast furnace, foundry, cupola, and for other industrial uses. Coke is produced during the heating of coal in the absence of air ; the process is called carbonization. Undergoing thermal decomposition, the light constituents of the coal are volatilized, and the heavier components crack, releasing hydrogen. The ash of the coal, as well as part of the sulfur, is contained in the carbonaceous residue, coke. The nature of the coke formed depends upon the original coal and the carbonization process employed. Coke may also be produced from other sources such as the delayed coking process which utilizes petroleum heavy residuals.

Although coke may vary greatly in physical form and chemical composition, a standard set of analyses is applicable to most samples. The analytical techniques for coke are almost identical to those for coal which are listed in Table VI-1. Differences which may occur in sample size and preparation are described in Section 3, dealing with actual methods. As an added note, although the analysis for chlorine in coal and coke is essentially the same, the chlorine content of coke is usually negligible and not required.

2. SAMPLING

A. Coal

It is of prime importance that coal samples be representative with respect to the bulk material. Obtaining a uniform sample is a difficult task due to the heterogeneous nature of coal. Detailed procedures for every situation are not available. However, several general objectives in sampling may be stated. Intended as guidelines in the planning of a sampling operation, they include:

1. The sample should be collected in a manner appropriate to the condition of the coal, e.g., sampling from a conveyor vis-a-vis from a rail car.

2. A gross sample from a lot of coal should be a composite of small increments.

3. The size and number of increments will depend upon the desired precision, as well as the nature of the coal itself.

4. The increments must be distributed throughout the lot to be sampled.

5. The number of gross samples depends upon the size of the lot.

6. The samples collected should be protected from loss of moisture, as well as contamination.

After collection of the gross sample, the material is air-dried under controlled conditions, i.e., humidity and temperature, if possible. (The loss of weight of the sample is also determined.) The air dried sample is then crushed to pass a No. 60 sieve (250 micron). A riffle - which is a sample divider - is then used to reduce the sample to about 50 g. After thorough mixing of the material, portions for the various analytical determinations are weighed and placed in appropriate containers. The above procedures are described in detail in ASTM D 2234, "Collection of a Gross Sample of Coal"[1], and ASTM D 2013, "Preparing Coal Samples for Analysis"[1]. A procedure for laboratory handling of samples is presented in the Bureau of Mines report, "Methods of Analyzing and Testing Coal and Coke"[2].

B. Coke

As with coal, bulk supplies of coke are nonhomogeneous, and require careful sampling procedures. The objective is to first obtain a gross sample representative of the bulk material, and then progressively reduce the weight for a laboratory sample. To carry out this procedure, the following general steps[1] should be followed:

1. Gross samples should be taken directly from the coke-conveying equipment, e.g., railroad car, supply bin. Samples generally should not be taken from the surface of the coke.

2. Increments for the gross sample should be taken systematically.

3. The gross sample is crushed and mixed, and the total weight is reduced to about 13.6 kg (30 lbs.) - .64 cm (1/4 inch) in size - for the laboratory sample.

4. A special moisture sample should be taken before crushing.

Coke samples are dried in the laboratory only if the samples are wet. The .64 cm (1/4 inch) size sample is mixed, reduced, and crushed to produce 50 grams of a sample passing a No. 60 sieve (250 micron). After mixing thoroughly, portions for the various analytical procedures are weighed. The described procedures are presented in detail in ASTM D 346, "Sampling Coke for Analysis"[1], ASTM D 271, "Laboratory Sampling and Analysis of Coal and Coke"[1], and in the Bureau of Mines report, "Methods of Analyzing and Testing Coal and Coke"[2].

3. ANALYSES

A. Coal

Due to the oxidation of coal, it is important that analyses be conducted as soon as possible after sample collection.

Table VI-2 provides a brief summary of pertinent methods and their applicability. In cases where more than one method may be suitable, the preferred method is listed first. The primary sources for these analyses are the ASTM procedures[1] and "Methods for the Analysis and Testing of Coal and Coke," set forth by the British Standards Institution (BSI)[4]. As mentioned previously, the former techniques are widely accepted in the United States and are, thus, listed as preferred methods. The BSI methods are generally the same as those proposed by the International Organization for Standardization. They are similar in the analytical approach to ASTM, although the actual techiques are somewhat different.

Descriptions of ultimate and proximate analyses are given in ASTM D 3172, "Proximate Analysis of Coal and Coke"[1], ASTM D 3176, "Ultimate Analysis of Coal and Coke"[1], and ASTM D 271, "Laboratory Sampling and Analysis of Coal and Coke"[1]. It is important that all analyses be reported on a consistent basis, with respect to sample moisture. Results are usually reported on an "as received" basis or on a "dry" basis. From a knowledge of the moisture, the calculation of one basis from the other is simple. However, it should be stressed that the basis upon which an analysis is reported must be specified.

B. Coke

The methods for analyzing coke are essentially the same as for coal (described in Table VI-2). Differences in technique may occur as the result of the coke's physical form or chemical composition and are noted. Deterioration of the sample is not usually considered a problem.

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.
2. "Methods of Analyzing and Testing Coal and Coke," U. S. Department of the Interior, Bureau of Mines, Washington, D. C., 1967.
3. "Solid Fuels - Power Test Codes," American Society of Mechanical Engineers, New York, New York, 154.
4. "Methods for the Analysis and Testing of Coal and Coke," British Standards Institution, London, England; BS 1016, Parts 3, 5, 6, and 8.

Table VI-1

ANALYSES FOR COAL AND COKE

SUMMARY LISTING

	PARAMETER	PREFERRED METHOD [a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS [b] (g)	COST OF ANALYSIS [c] ($)	SRM AVAILABLE [d]
1.	Sulfur	ASTM D 3177	0.1 - 1.0	5 - 15	SF-1
2.	Carbon (Total) and Hydrogen	ASTM D 3178	0.2	20 - 30	
3.	Nitrogen	ASTM D 3179	1.0	15 - 25	
4.	Ash	ASTM D 3174	1.0	5 - 15	SF-1
5.	Volatile Matter	ASTM D 3175	1.0	5 - 15	
6.	Moisture	ASTM D 3173	1.0	4 - 15	
7.	Chlorine	ASTM D 2361	1.0	NA	
8.	Gross Calorific Value	ASTM D 2015	1.0	10 - 20	SF-5
9.	Oxygen	ASTM D 3176	NP [e]	---	
10.	Fixed Carbon	ASTM D 3172	NP [f]	---	

NP - Not Pertinent; NA - Not Available

a. Specific references to methods listed are given in Table VI-2.
b. These are the sample requirements for a single analysis.
c. Estimated range based on prices charged by analytical service laboratories in early-1977. Prices for proximate and ultimate analyses are always quoted - they range from $20 to $40 and $40 to $100, respectively - but the analyses are not always the same as those listed in the test.
d. See Appendix A for details.
e. Determined by difference from ultimate analysis.
f. Determined by difference from proximate analysis.

Table VI-2

METHODS OF ANALYSIS FOR COAL AND COKE

	SUGGESTED METHOD(S)				
PARAMETER	No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
1. Sulfur	A. ASTM D 3177 (See Note #1)	1	Eschka Method: Sample is ignited with Eschka mixture in air at 800°C for 1.5 hours. Ingition of coke may require additional time. After extraction with hot water, $BaCl_2$ is used to precipitate $BaSO_4$. Sulfur is determined gravimetrically after filtration.	Coal and coke.	(P) **Repeatability:** Coal (< 2% S) - 0.05% Coal (> 2% S) - 0.10% Coke - 0.03% **Reproducibility:** Coal (< 2% S) - 0.10% Coal (> 2% S) - 0.20% Coke - 0.05%
			Bomb-Washing Method: Washings from bomb calorimeter are treated in manner similar to Eschka Method. References: ASTM D 2015/D 3286, Gross Calorific Value of Solid Fuel.	Coal and coke.	
	B. BS 1016 Part 6 (See Note #2)	2	High Temperature Method: Sample is burned at 1350°C in oxygen current for four minutes. Sulfur is converted to oxides and absorbed in H_2O_2 to form H_2SO_4 (which is titrated with sodium borate). Acidity due to HCl is deducted.	Coal and coke.	(P) **Repeatability:** 0.05% **Reproducibility:** 0.10%
2. Carbon (Total) and Hydrogen	A. ASTM D 3178 (See Notes #3, #4, and #5)	1	Combustion of sample occurs under oxygen flow, at 850°C to 900°C, for up to 30 minutes. H_2O and CO_2 are trapped in sampling train with appropriate absorbents.	Coal and coke.	(P) **Repeatability:** Carbon - 0.3% Hydrogen - 0.07%
	B. BS 1016 Part 6 (See Note #6)	2	This method is similar to the ASTM procedure, but combustion is controlled at 1350°C.	Coal and coke.	(P) **Repeatability:** Carbon - 0.25% Hydrogen - 0.12% **Reproducibility:** Carbon - 0.50% Hydrogen - 0.25%

All notes appear at the end of this table.

Table VI-2

METHODS OF ANALYSIS FOR COAL AND COKE

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
3. Nitrogen	A. ASTM D 3179	1	Kjeldahl-Gunning Method: 1g sample is digested in H_2SO_4 for three to six hours with heating. Coke may require 12 to 16 hours. Ammonia is distilled into H_2SO_4 solution and titrated. An alternate approach uses boric acid in place of H_2SO_4.	Coal and coke. (Coke is ground to smaller particle size.)	(P) **Repeatability:** 0.05%
	B. BS 1016 Part 6 (See Note #7)	2	Semi-micro Kjeldahl: 0.1 g sample is treated in a similar manner to the previous method (with boric acid).	Coal and coke.	(P) **Repeatability:** 0.05% **Reproducibility:** 0.10%
4. Ash	A. ASTM D 3174 (See Notes #8, #9, and #10)	1	Sample is ignited in an open crucible at 700°C to 750°C until constant weight is attained. Coke is ignited at 950°C.	Coal and coke.	(P) **Repeatability:** 0.2% to 0.5% **Reproducibility:** 0.3% to 1.0%
	B. BS 1016 Part 3	3	Sample is ignited at 815°C.	Coal and coke.	(P) **Repeatability:** 0.15% to 0.25% **Reproducibility:** 0.3% to 0.5%
5. Volatile Matter	A. ASTM D 3175	1	Sample is heated in a covered crucible at 950°C for seven minutes. A modified method is employed for sparking coals as well as some cokes.	Coal and coke.	(P) **Repeatability:** Coal - 0.3% to 1.0% Coke - 0.2% to 0.5% **Reproducibility:** Coal - 0.6% to 2.0% Coke - 0.4% to 1.0%
	B. BS 1016 Part 3	3	Sample is heated at 900°C for seven minutes.	Coal and coke.	(P) **Repeatability:** 0.2% to 0.3% **Reproducibility:** 0.5% to 1.0%

Table VI-2

METHODS OF ANALYSIS FOR COAL AND COKE

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
6. Moisture	A. ASTM D 3173	1	Sample is dried in oven at 104°C to 110°C for one hour, under a stream of dry air. This is an indirect method, dependent upon the weight loss of the sample.	Coal and coke.	(P) **Repeatability:** 0.2% to 0.3% **Reproducibility:** 0.3% to 0.5%
	B. BS 1016 Part 3 (See Note #11)	3	Sample is dried in oven at 104°C to 110°C for one hour, under a stream of nitrogen. The determination may be indirect (as described above), or direct by measuring the moisture contained in an absorption tube.	Coal and coke.	(P) **Repeatability:** 0.10% to 0.15%
7. Chlorine	A. ASTM D 2361	1	Oxygen Bomb Method: Sample is burned with Eschka mixture in a bomb with oxygen. Eschka Method: Sample is heated with Eschka mixture in oxidizing atmosphere at 675°C for 1.5 hours. In both methods, chloride is determined by titration, either colorimetrically or potentiometrically.	Coal and coke.	(P) **Repeatability:** 0.03% **Reproducibility:** 0.06%
	B. BS 1016 Part 8	4	The same procedure is followed as in the sulfur determination of BS 1016, Part 6. HCl is determined by titration.	Coal and coke.	(P) **Repeatability:** (< 4%) - 0,02% (> 4%) - 0.05% **Reproducibility:** (< 4%) - 0.02% (> 4%) - 0.05%

Table VI-2

METHODS OF ANALYSIS FOR COAL AND COKE

(continued)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
8. Gross Calorific Value	A. ASTM D 2015 (See Note #12)	1	Adiabatic Bomb Calorimeter Method: Sample is burned in oxygen and calorific value determined from temperature rise.	Solid fuels.	
	B. ASTM D 3286 (See Note #12)	1	Isothermal-Jacket Bomb Calorimeter Method: Sample is burned in oxygen and calorific value is determined from temperature readings and other heat sources.	Solid fuels.	
	C. BS 1016 Part 5 (See Notes #12 and #13)	5	Method is similar to ASTM procedures, using adiabatic, isothermal, or static calorimeter.	Coal and coke.	(P) Repeatability: 29 cal/g Reproducibility: 72 cal/g

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*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference of duplicate results submitted by two or more laboratories. The original reference should be checked if precision is critical since the wording may imply special conditions for the applicability of the precision numbers given.

Notes for Table VI-2:

1. There is a titrimetric alternative to the gravimetric method, involving precipitation with barium chromate and subsequent iodometric determination of remaining chromate. Reference: International Standard 334, Coal and Coke - Determination of Sulphur - Eschka Method.

2. This method is useful for rapid results, or for a large number of determinations. The chlorine content of the sample is determined at the same time as sulfur.

3. This is sometimes called the Liebig Method.

4. Nitrogen dioxide is produced, introducing an error in the carbon determination.

5. It is necessary to correct for hydrogen originally present as moisture in the sample.

6. Nitrogen dioxide is not produced at this high temperature.

7. The macro-method requiring 1 g of sample is necessary where bands of varying nitrogen composition occur in coal seams.

8. For low ash coke, a large sample size of 5 g may be necessary.

9. There is a modified ASTM procedure for samples high in calcite and/or pyrite.

10. The ash content must be corrected for sample moisture, if a pre-dried sample is not used.

11. The use of nitrogen in place of air prevents oxidation of the sample.

12. Corrections must be applied for heats of formation of H_2SO_4 and HNO_3.

13. In the case of certain cokes, a correction for unburned carbon may be required.

CHAPTER VII

REFUSE-DERIVED SOLID FUELS (RDSF) AND PEAT

1. INTRODUCTION/SUMMARY

A. Refuse-Derived Solid Fuels

Refuse-derived solid fuels (RDSF) are taken here to primarily include processed municipal refuse; the processing may include magnetic separation, shredding, air classification, chemical treatment, milling or other such processes. It is not the intent of this chapter to cover methods applicable to raw (unprocessed) municipal refuse. Also the methods covered here for RDSF are not intended to be applicable to refuse-derived liquid fuels, industrial refuse-derived fuels, or agricultural and forestry wastes.

RDSF may be used as the sole fuel in a heat-generating process, or it may be used as a supplementary fuel. Several systems are currently operational and several publicly and privately-sponsored research projects are ongoing. The use of RDSF is likely to grow signficantly in the years to come.

Table VII-1 gives a summary listing of the fuel analyses that are important for RDSF combustion, along with an identification of the preferred method of analysis and other information relating to the analyses. Additional information on the methods of analysis, including alternate methods for most parameters, is given in Section 3 of this chapter. All of the methods discussed are either from the American Society for Testing and Materials (ASTM) methods for coal and coke[1], ASTM methods for peat[5], Bureau of Mines methods for coal and coke[3], or U. S. Environmental Protection Agency (EPA) methods for solid waste[2]. While only the EPA methods were developed for specific application to RDSF (and other solid wastes), both the ASTM and the Bureau of Mines methods for the more common parameters have been successfully used to characterize RDSF.

It should be recognized that there is currently no generally accepted set of standard analytical methods for the characterization of RDSF. The EPA has, however, recently contracted with the ASTM (E38.01 Energy Subcommittee) to develop such a set of standard methods for the sampling and analysis of RDSF. Tentative standard methods may be available in about two years. Final approval by ASTM may require additional time.
It is expected that a significant number of methods will be modifications of the existing ASTM methods for coal and coke. Because of this expectation, and because the ASTM methods for coal and coke seem to be generally applicable to RDSF, they have been listed as the preferred method for all methods covered in their manual. Their principal weakness may be that test sample sizes may be too small for RDSF(that is not sufficiently homogeneous) resulting in erratic results on replicate samples. In such cases, sample sizes should be increased (when possible) to allow the use of a representative portion.

Environmental assessments of processes using RDSF will need to include additional fuel analyses beyond those covered in this manual. Those likely to be required include: microbiological tests (including tests for pathogenic organisms); trace elements in the fuel and in the ash; soluble portions of the fuel (especially chloride and alkalies) and the ash; trace organics in fuel leachate; odor; and, possibly, tests to determine the biological stability of the stored fuel.

B. Peat

According to the ASTM definition given in D 2607[5]:

> "The term peat refers only to organic matter of geologic origin, excluding coal, formed from dead plant remains in water and in the absence of air. It occurs in a bog, swampland, or marsh, and it has an ash content not exceeding 25% by dry weight."

Peat may appear to consist solely of fibrous material, even after it has been shredded and milled. Minimum fiber contents (based on oven-dried weights) are given for various classifications of peat in ASTM D 2607[5].

Currently, peat is not used commercially as a fuel in the United States, though significant deposits do occur in several of the north-central states. It is used widely as a fuel in Ireland and Russia.

Table VII-2 gives a summary listing of the fuel analyses that are important for peat combustion, along with an identification of the preferred method of analysis and other information relating to the analyses. Additional information on the methods of analysis, including alternate methods for most parameters is given in Section 3 of this chapter. All of the methods discussed are either from ASTM methods for coal and coke[1], ASTM methods for peat[5], Bureau of Mines methods for coal and coke[3], or EPA methods for solid waste[2]. Only the methods (preferred methods in Table VII-2) for nitrogen, moisture, ash, organic matter, and sieve analysis were specifically developed for peat. With regard to the other methods, no data were available indicating the preferred methods were applicable. But, again, the choice seems reasonable. As with RDSF, the chief weakness of the methods that are not intended for peat analyses may be inadequate sample size. When working with peat that is not sufficiently homogeneous, the sample sizes for these analyses should be increased, if possible.

Environmental assessments of processes using peat will need to include additional fuel analyses beyond those covered in this manual. Those likely to be required include: trace elements in the fuel and in the ash; soluble portions of the fuel and the ash (especially chloride and alkalies); and, possibly, tests to determine the biological stability of the stored fuel.

2. SAMPLING

A. Refuse-Derived Solid Fuels

Sample collection and preparation must be given careful attention for RDSF. The objectives of any sampling program should include:

1. The collection of representative (bulk) samples;
2. Statistical sub-sampling to convenient working weights;
3. Preparation of a dry, uniform-textured material; and,
4. Disease control.

RDSF (taken here to be a processed municipal refuse) in its as-fired form may lack any real homogeneity,and its composition may vary on both a daily and seasonal basis.

Procedures for collecting gross samples of RDSF will have to be tailored to (1) the nature of the material being sampled; (2) the nature of the fuel-processing/handling equipment; and, (3) the precision and accuracy requirements of the analyses to be carried out. Relatively simple grab samplings may suffice for some purposes; the total sample should be the composite of several grab samples spread out, both in space (e.g., different portions of a stroage pile) and time. One description of such methods is given in the Bureau of Mines report, "Characterizing Combustible Portions of Urban Refuse for Potential Use as Fuel"[4]. When more precision is required in the gross sample, the methods described in ASTM D 2334, "Standard Methods for Collection of a Gross Sample of Coal"[1], may be applicable with only slight modification; Section 8 and Appendices A-1 and A-2 of this method are especially pertinent.

The preparation of a laboratory sample from a gross sample usually involves three basic operations: (1) drying; (2) grinding or pulverizing; and, (3) mixing. Procedures adequate for the preparation of a laboratory sample of RDSF are given in several sources. The procedures of ASTM D 2013, "Standard Method for Preparing Coal Samples for Analysis"[1], and ASTM D 271, "Standard Methods of Laboratory Sampling and Analysis of Coal and Coke"[1], are considered acceptable. In addition, the procedures given for the preparation of a laboratory sample of coal by the Bureau of Mines[3] and for the preparation of a laboratory sample of solid waste-related materials by the EPA[2] are suitable. Of all these methods, only those given by the EPA are specifically intended for use with RDSF. It should be noted that most of the ASTM analytical methods specify the type of sample to be used, including reference to a specific sample preparation procedure.

None of the above mentioned methods give any detailed consideration to disease control, though suggestions are given[2,4] that the outside of the sample collection bags be sprayed with Lysol® and that the collectors and analysts wear gloves (e.g., neoprene-coated canvas), and, possibly, face masks. Face masks, such as surgical masks, are recommended when working with RDSF in the finely divided form[2]. The health risks associated with handling municipal refuse are not well documented and there appear to be no regulations for worker protection. Tetanus inoculation is one additional precaution that could be taken. Additionally, special care should be taken in handling material known to contain hospital wastes; this material could, in addition, be sterilized by various procedures.

B. Peat

Sampling methods for peat are given in ASTM D 2944, "Standard Method of Sampling Peat Materials"[5]. This method covers procedures for obtaining samples for use in the determination of moisture, ash, organic matter, nitrogren, particle size range, and other parameters not covered in this manual. For parameters other than the above, it may be necessary to use the ASTM, Bureau of Mines, or EPA methods for the preparation on a laboratory sample* since they will yield a more homogeneous sample better suited for those analyses where only small quantities are used.

3. ANALYSES

A. Refuse-Derived Solid Fuels

Table VII-3 gives, for each parameter of interest, additional information on the method(s) of analysis deemed suitable. When more than one method is listed, the preferred method is given first. The parameters are listed in the order given in Table VII-1.

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*See Section 2-A above for titles of and references to these methods.

Three generally applicable comments should be considered. First, where ASTM methods for coal and coke have been listed, the sample requirements are generally small (see Table VII-1). These sample sizes may be inadequate for RDSF that is not as homogeneous as a similarly processed sample of coal. Thus, sample sizes may need to be increased in some cases and appropriate adjustments made in the analytical procedure. Additionally, larger sample sizes would be preferable for the determination of the calorific value of RDSF because their values are roughly half of those of the more common fuels (e.g., coal, fuel oil). This can lead to additional difficulty in the precise determination of temperature changes required in the method. In this particular case, care should be taken not to increase the sample size beyond the safe capacity of the bomb being used.

Second, caution should be used in the comparison of any precision information given in Table VII-3 that derives from tests on coal and coke. The homogeneity of the sample may not be comparable, and even if it was, the values given in Table VII-3 may not apply where the absolute values of the parameter being measured in RDSF are significantly different from those in coal and coke. Such is the case, for example, with the calorific value.

Third, because the moisture content of RDSF may be highly variable - and high on an absolute scale as well - it is suggested that analytical results be reported on a "moisture-free" basis. The moisture-free sample is one that has been dried at elevated temperatures (approximately 105°C) in a manner such as is specified in either ASTM D 3173 or D 2974.

B. Peat

Information on all except two of the preferred methods of analysis for peat (as listed in Table VII-2) is given in Table VII-3. Thus, Table VII-3 should be used for all of the peat analyses except nitrogen and size distribution. Equivalent information for these two parameters is given in Table VII-4.

The cautionary statements given above in Section 3-A for RDSF are also applicable to peat. This holds especially for the variability (and high values) of the moisture content and the resulting need to report all other analyses on a moisture-free basis.

4. REFERENCES

1. "Annual Book of ASTM Standards (1974) - Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.

2. Bender, D. F., Peterson, M. L., and Stierli, J. (eds.), "Physical, Chemical and Microbiological Methods of Solid Waste Testing," U. S. Environmental Protection Agency, Cincinnati, Ohio; May, 1973.

3. "Methods of Analyzing and Testing Coal and Coke," U. S. Department of the Interior, Bureau of Mines, Washington, D. C., 1967.

4. Schultz, H., Sullivan, P. M., and Walker, F. E., "Characterizing Combustible Portions of Urban Refuse for Potential Use as Fuel," U. S. Department of the Interior, Bureau of Mines Report of Investigations, RI 8044, 1975.

5. "Annual Book of ASTM Standards (1974): Part 19: Natural Building Stones; Soil and Rock; Peats, Mosses and Humus," American Society for Testing and Materials, Philadephia, Pennsylvania.

Table VII-1

ANALYSES FOR REFUSE-DERIVED SOLID FUELS

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (g)	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Carbon (Total) and Hydrogen	ASTM D 3178	0.2	20 - 30	
2. Nitrogen	ASTM D 3179	1.0	15 - 25	SF-4
3. Sulfur	ASTM D 3177	1.0	5 - 15	
4. Oxygen	ASTM D 271	NP	---	
5. Chlorine	ASTM D 2361	1.0	NA	
6. Moisture	ASTM D 3173	1.0	4 - 15	
7. Volatile Matter	ASTM D 3175	1.0	5 - 15	
8. Ash	ASTM D 3174	1.0	5 - 15	
9. Ash Fusibility	ASTM D 1857	3-5 (of ash)	15 - 25	
10. Apparent Density	ASTM D 291 (Procedure A)	∿ 35 kg	5 - 10	
11. Sieve Analysis	ASTM D 410	min. 45 kg	4 - 12	
12. Calorific Value	ASTM D 2015	1.0	10 - 20	SF-5
13. Carbonate Carbon	ASTM D 1756	5.0	NA	

NP - Not Pertinent; NA - Not Available.

[a] All ASTM methods are given in Reference #1.

[b] These are the sample requirements for a single analysis of coal or coke and may be significantly different from the amount of RDSF needed. Greater amounts of RDSF may be required for samples with little homogeneity. The amounts required by a laboratory may also be larger for a variety of reasons, including those connected with sample preparation.

[c] Estimated ranged based on prices charged by one or more service laboratories for coal analyses in early-1977.

[d] See Appendix A for details.

Table VII-2

ANALYSES FOR PEAT

SUMMARY LISTING

PARAMETER	PREFERRED METHOD[a]	APPROXIMATE AMOUNT OF SAMPLE NEEDED FOR ANALYSIS[b] (g)	COST OF ANALYSIS[c] ($)	SRM AVAILABLE[d]
1. Carbon (Total) and Hydrogen	ASTM D 3178	0.2	20 - 30	
2. Nitrogen	ASTM D 2973	1.0	15 - 25	SF-4
3. Sulfur	ASTM D 3177	1.0	5 - 15	
4. Oxygen	ASTM D 271	NP	---	
5. Chlorine	ASTM D 2361	1.0	NA	
6. Moisture	ASTM D 2974 (Method II)	100-300	4 - 15	
7. Organic Matter	ASTM D 2974	10.	5 - 15	
8. Ash	ASTM D 2974	10.	5 - 15	
9. Ash Fusibility	ASTM D 1857	3-5 (of ash)	15 - 25	
10. Apparent Density	ASTM 291 (Procedure A)	∿ 35 kg	5 - 10	
11. Sieve Analysis	ASTM D 2977	100-300	4 - 12	
12. Calorific Value	ASTM D 2015	1.0	10 - 20	SF-5
13. Carbonate Carbon	ASTM D 1756	5.0	NA	

NP - Not Pertinent; NA - Not Available

[a] All ASTM methods are given in Reference #1.

[b] These are the sample requirements for a single analysis of coal or coke and may be significantly different from the amount of peat needed. Greater amounts of peat may be required for samples with little homogeneity. The amounts required by a laboratory may also be larger for a variety of reasons, including those connected with sample preparation.

[c] Estimated range based on prices charged by one or more service laboratories for coal analyses in early-1977.

[d] See Appendix A for details.

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

	SUGGESTED METHOD(S)				
PARAMETER	Title/No.	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
1. Carbon (Total)	A. ASTM D 3178 (See Notes #1 and #2)	1	A weighed sample is burned in a closed system and the products of combustion fixed in an adsorption train. CO_2 adsorber may contain NaOH, KOH or soda lime. Moisture adsorber is anhydrous magnesium perchlorate ($Mg(ClO_4)_2$).	Method developed for coal and coke. Should be adequate for RDSF.	(P) Unknown for RDSF. For coal and coke: **Repeatability:** Carbon - 0.3% Hydrogen - 0.07%
	B. EPA	2	Essentially similary to ASTM D 3178, but with additional components in the combustion train to insure complete combustion of certain chemicals and to remove undesirable products of combustion.	Generally applicable to dry solid waste samples containing 0.5% to 83.0% carbon and 0.01% to 7.8% hydrogen. Modifications required for samples with high values of As, Sb, Bi, or Hg.	(A) Carbon determined within 1% of true value; hydrogen within 2% to 4%. (P) See data given in Reference #2. Tests showed standard deviations for duplicate samples to be in the following ranges: Carbon - 0.04% to 0.22% Hydrogen - 0.04% to 0.22%
2. Nitrogen	A. ASTM D 3179 (See Notes #1, #2, #3, and #4)	1	Analysis is by either the Kjeldahl-Gunning or an alternative method. In both, nitrogen is converted to ammonium salts which are subsequently decomposed; ammonia is recovered by distillation and finally determined by alkalimetric or acidimetric titration.	Method developed for coal and coke. Should be adequate for RDSF.	(P) Unknown for RDSF. For coal and coke: **Repeatability:** 0.05%
	B. EPA-Kjeldahl	2	Kjeldahl method is similar to that in ASTM D 3179.	Applicable to RDSF if nitrogen content is primarily organic and/or ammoniacal.	(A) Tests on SRM's** always yielded > 98.5% recovery. (P) See data given in Reference #2. Tests showed standard deviations on replicate samples to range from 0.01% to 0.12%.

All notes appear on the last page of this table.

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERVIED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S) Title/No.	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
2. Nitrogen (continued)	C. EPA Comprehensive	2	This is a modified Kjeldahl procedure where nitrates are first reduced wtih metallic chromium in an acid medium.	Applicable to RDSF, especially for those with high chloride-nitrate ratios.	(A) Tests on SRM's always yielded > 98.2% recovery. (P) See data given in Reference #2. Tests showed standard deviations on replicate samples to range from 0.01% to 0.14%.
	D. EPA	2	An instrumental method in which the sample is decomposed at high temperatures in the absence of air and with the aid of oxidizing agents. All nitrogen reduced to N_2 and, after removal of CO_2, is measured volumetrically. (Analysis time ∿ 15 minutes.)	Applicable to RDFS, including samples with high nitrate contents.	(A) Tests on SRM's always yielded > 99% recovery. (P) See data given in Reference #2. Tests showed standard deviations on replicate samples to be in the range of 0.00% to 0.10%.
3. Sulfur	A. ASTM D 3177 (See Notes #1, #2, and #4)	1	Bomb Washing Method: Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination (ASTM D 2015).	Method developed for coal and coke. Should be adequate for RDSF.	(P) Unknown for RDSF. For coal and coke: Repeatability: Coal (< 2% S) - 0.05% Coal (> 2% S) - 0.10% Reproducibility: Coal (< 2% S) - 0.10% Coal (> 2% S) - 0.20%
	B. ASTM D 3177 (See Notes #1, #2, and #4)	1	Eschka Method: Sulfur is determined as $BaSO_4$ after sample is heated (with the Eschka mixture) in a controlled manner and sulfur containing residue extracted with hot water. $BaCl_2$ is used to precipitate the sulfur. (The method is more time consuming than the bomb washing method.)	Method developed for coal and coke. Should be adequate for RDSF. Bureau of Mines Eschka method (see Reference #3) has been used successfully on RDSF (see Reference #4).	(P) Same as for bomb washing method.

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S) Title/No.	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
4. Oxygen	A. ASTM D 271 (See Note #2)	1	Determined indirectly by subtracting from 100 the percentages of hydrogen, carbon, sulfur, nitrogen, moisture, and ash.	Method developed for coal and coke. Should be applicable for RDSF.	Not known
	B. EPA	2	Determined indirectly from known values for total carbon, carbonate carbon in sample, carbonate carbon in ash, hydrogen, nitrogen, sulfur, chlorine, and volatiles (or ash).	Applicable for RDSF.	(P) Inspection of past data, by EPA, indicates precision should be within 1% to 2%.
5. Chlorine	A. ASTM D 2361 (See Notes #2 and #4)	1	Sample oxidized either in an Eschka combustion apparatus or a bomb containing oxygen under pressure. Combustion residue is collected in acid solution and chlorine determined by potentiometric titration or by modified Volhard procedure.	Method developed for coal. Should be applicable for RDSF. Bureau of Mines (see Reference #3) has been used successfully on RDSF (see Reference #4).	(P) Unknown for RDSF. For coal: Repeatability: 0.03% Reproducibility: 0.06%
	B. EPA	2	Sample is oxidized in a bomb containing oxygen under pressure. Combustion products adsorbed in a carbonate solution are acidified and titrated with mercuric nitrate.	Applicable to RDSF. Iodine and bromine, if present, will add to chlorine result. Chromate and sulfate interfere when present in excess of 10 mg/1, as will ferric ions in excess of 20 mg/1.	(A) EPA tests with SRM's had mean recoveries of about 98%. (P) See data give in Reference #2. Tests showed standard deviations on replicate sample to range, with one exception, from 0.01% to 0.04%.
6. Moisture	A. ASTM D 3173 (See Notes #1 and #2)	1	Moisture is determined by measuring the weight loss in a sample after heating in an oven, through which dry air is circulated, for one hour.	Method developed for coal and coke. Should be applicable for RDSF. (1 g test specimen used.) Bureau of Mines method (see Reference #3) has been used successfully on RDSF (see Reference #4).	(P) Unknown for RDSF. For coal and coke: Repeatability: Coals (< 5% moisture) - 0.2% Coals (> 5% moisture) - 0.3% Reproducibility: Coals (< 5% moisture) - 0.3% Coals (> 5% moisture) - 0.5%

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S)		SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
	Title/No.	Ref.			
6. Moisture (continued)	B. ASTM D 2974 (See Note #4)	5	An as-received or air-dried sample is heated in the open air at 105°C for 16 hours.	Method developed for peat. Should be applicable for less homogeneous samples of RDSF where larger samples must be used. (10 g test specimen used.)	Not given
7. Volatile Matter	A. ASTM D 3175 (See Notes #1 and #2)	1	Volatile matter is determined from the weight loss after sample is heated in an oven at 950° ± 20°C for seven minutes. A modification for sparking samples is prescribed. Crucible with sample is kept covered to keep air out.	Method developed for coal and coke. Should be applicable for RDSF. Only volatile hydrocarbons are measured.	(P) Unknown for RDSF. For other materials: **Repeatability:** Ranges from 0.2% for coke up to 0.7% for low grade coal and 1% for lignite and peat. **Reproducibility:** Ranges from 0.4% for coke up to 1.4% for low grade coal and 2% for lignite and peat.
	B. EPA	2	Volatile matter is determined from the weight lose after the sample is heated in an oven at 600°C (achieved gradually) for two hours. Crucible are left open (lids are tilted) to allow air circulation over samples.	Applicable for RDSF. Method allows the oxidation of elemental carbon.	(A) EPA tests with SRM's showed yields between 99.92% and 100.45%. (P) See data given in Reference #2. Tests showed standard deviations on replicate combustible refuse sample to range from 0.2% to 2.2%.
	C. ASTM D 2794	5	"Organic Matter" determined from weight loss of sample heated at 550°C (in an uncovered dish) in an oven.	Method developed for peat. Should be applicable for RDSF.	Not given

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S) Title/No.	Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
6. Moisture (continued)	B. ASTM D 2974 (See Note #4)	5	An as-received or air-dried sample is heated in the open air at 105°C for 16 hours.	Method developed for peat. Should be applicable for less homogeneous samples of RDSF where larger samples must be used. (10 g test specimen used.)	Not given
7. Volatile Matter	A. ASTM D 3175 (See Notes #1 and #2)	1	Volatile matter is determined from the weight loss after sample is heated in an oven at 950° ± 20°C for seven minutes. A modification for sparking samples is prescribed. Crucible with sample is kept covered to keep air out.	Method developed for coal and coke. Should be applicable for RDSF. Only volatile hydrocarbons are measured.	(P) Unknown for RDSF. For other materials: **Repeatability:** Ranges from 0.2% for coke up to 0.7% for low grade coal and 1% for lignite and peat. **Reproducibility:** Ranges from 0.4% for coke up to 1.4% for low grade coal and 2% for lignite and peat.
	B. EPA	2	Volatile matter is determined from the weight loss after the sample is heated in an oven at 600°C (achieved gradually) for two hours. Crucible are left open (lids are tilted) to allow air circulation over samples.	Applicable for RDSF. Method allows the oxidation of elemental carbon.	(A) EPA tests with SRM's showed yields between 99.92% and 100.45%. (P) See data given in Reference #2. Tests showed standard deviations on replicate combustible refuse sample to range from 0.2% to 2.2%.
	C. ASTM D 2794	5	"Organic Matter" determined from weight loss of sample heated at 550°C (in an uncovered dish) in an oven.	Method developed for peat. Should be applicable for RDSF.	Not given

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S) Title/No.	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)*
11. Sieve Analysis	A. ASTM D 410	1	Sample is passed through a series of sieves, largest first, and the amount retained on each sieve weighed.	Method developed for bulk samples of coal. Should be applicable for bulk samples of RDSF that have not been finely shredded.	(P) Unknown for RDSF. For coal, sum of weights should be within 2% of initial sample weight.
	B. ASTM	1	Samples are sieved successively with a series of sieves, smallest first, and the amount retained on each sieve weight.	Method developed for pulverized coal. Should be applicable for finely shredded RDSF having no particle ≥ 0.32 cm (1/8").	(P) Unknown for RDSF. For coal: Repeatability: 1% on all sizes Reproducibility: 3% on No. 200 sieve
12. Calorific Value	A. ASTM D 2015 (See Notes #4 and #6)	1	A weighed sample is burned in an adiabatic bomb calorimeter and the calorific value determined from temperature observations made before and after combustion. Thermometer and thermochemical corrections are required.	Method developed for solid fuels and should be applicable to RDSF.	(P) Unknown for RDSF. For 60-mesh pulps (see D 2015 in Reference #1). Repeatability: 27.8 cal/g (50 Btu), dry basis Reproducibility: 55.6 cal/g (100 Btu), dry basis
	B. ASTM D 271 (See Notes #2 and #6)	1	A weighed sample is burned in a bomb calorimeter and the calorific value determined from temperature and time observations made before, during, and after combustion. Thermometer and thermochemical corrections are required.	Method developed for coal and coke. Should be applicable to RDSF. Bureau of Mines method (see Reference #3) has been used successfully on RDSF (see Reference #4).	(P) Unknown for RDSF. For coal and coke: Repeatability: 27.8 cal/g (50 Btu), dry basis Reproducibility: 55.6 cal/g (100 Btu), dry basis
	C. EPA Total Heat of Combustion (See Note #6)	2	Method uses Parr adiabatic calorimeter in a manner similar to that given in ASTM D 2015.	Applicable to RDSF with particle size less than 2 mm.	(A) EPA tests with SRM's gave average value 1.2% from true value. (P) See data given in Reference #2. Tests showed standard deviations of duplicate (combustible) refuse samples were 42 cal/g (76 Btu/lb).

Table VII-3

METHODS OF ANALYSIS FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(continued)

PARAMETER	SUGGESTED METHOD(S) Title/No.	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)
13. Carbonate Carbon	A. ASTM D 1756	1	Carbonate carbon is determined as carbon dioxide by decomposing, with hydrochloric acid, a weighed sample in a closed system. The evolved carbon dioxide is absorbed in an absorbent (NaOH or KOH on an inert carrier). The increase in weight of the absorbent is measured, and the carbon dioxide content of the sample determined from this figure.	Method developed for coal. Should be applicable to RDSF.	(P) Unknown for RDSF. For coal: Repeatability: 0.05% for CO_2 < 1% 0.10% for CO_2 > 1% Reproducibility: 0.10% for CO_2 < 1% 0.20% for CO_2 > 1%
	B. EPA	2	Carbonate carbon is determined gravimetrically after reacting the sample with hydrochloric acid and fixing the evolved gases in an adsorption train. CO_2 from the carbonate carbon is adsorbed in Nesbitt bulbs (containing Indicard and activated alumina).	Applicable for RDSF. Good results achieved on samples with carbonate contents from 0.05% to 8.0%.	(A) EPA tests with SRM's had average yield of 99.7%. (P) See data given in Reference #2. Tests showed standard deviation for duplicate analyses on portions of refuse ranged from 0.01% to 0.18%.

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*Precision, when known, is usually given as either repeatability and/or reproducibility. The number given for repeatability is the acceptable difference for duplicate results by the same laboratory; that for reproducibility is the acceptable difference for duplicate results submitted by two or more laboratories. The original references should be checked if precision is critical since the wording may imply special conditions for the applicability of the precision numbers given.

**SRM: Standard Reference Materials.

Notes for Table VII-3:

1. Method also given in ASTM D 271. (See Reference #1.)

2. A similar method is specified in the Bureau of Mines publication, "Methods of Analyzing and Testing Coal and Coke". (See Reference #3.)

3. An additional alternative method for the analysis of nitrogen in RDSF is given in ASTM D 2973, "Standard Method of Test for Total Nitrogen in Peat Materials"[5]. The method is similar to the ASTM D 3179 ("alternative") method with the major difference being that D 2973 requires a 10 g tests sample versus a 1 g test sample for D 3179. Data from duplicate analyses of RDSF by this method (D 2973) are given in Appendix D.

4. Data from analyses of a RDSF by this method are given in Appendix D.

5. A compact apparent density may also be determined by applying a 9.07 kg (20 pound) plunger, 30.48 cm × 30.48 cm (12" × 12") to the top of the box containing the sample. When this is done, the vertical dimensions of the compacted sample must be measured to determine the volume.

6. These methods determine the *gross* calorific value which is obtained under conditions of constant volume. It is often desired to have the *net* calorific value which is the value corresponding to combustion at atmospheric pressure, under conditions such that all water in the products remains in the form of vapor. The net calorific value may be calculated from the gross calorific value, as described in ASTM D 407[1].

Table VII-4

METHODS OF ANALYSIS FOR PEAT - SUPPLEMENTARY LISTING

(See Table VII-3 for information on other specified analyses for peat.)

PARAMETER	SUGGESTED METHOD(S) No./Title	SUGGESTED METHOD(S) Ref.	SUMMARY OF METHODS	APPLICABILITY	ACCURACY (A) AND PRECISION (P)
1. Nitrogen	ASTM D 2973	5	Nitrogen is converted into ammonium salts by destructive digestion and, subsequently, decomposed in a hot alkaline solution from which the ammonia is recovered by distillation and finally determined by acidimetric titration.	Method developed for peat.	Not given
2. Size Distribution	ASTM D 2977	5	An air-dried sample is separated into four designated fractions by means of an 8-mesh and a 20-mesh sieve. One fraction consists of foreign matter removed manually from the 8-mesh sieve.	Method developed for peat. Will not be adequate for finely milled peat.	Not given

APPENDIX A

AVAILABLE STANDARD REFERENCE MATERIALS

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1. INTRODUCTION

Reference materials are mixtures or pure substances which have been prepared or analyzed in such a way that the concentrations of particular elements in these materials, or particular physical properties, are known accurately. Such materials of known composition are often used in commerce and other fields to establish the accuracy of new chemical and physical analysis methods. In addition, analysis of those materials allows assessment of the performance of the analysts carrying out the tests. Submission of portions of appropriate reference materials as part of a sample set can also constitute a type of quality assurance program on analyses being performed. This can be of particular use when the analytical laboratory is remote from the group originating the samples.

2. TYPES OF REFERENCE MATERIALS

There are various types or classes of reference materials which can be used to check on the accuracy and precision of analyses.

Those substances which are most accurately characterized, either by preparation or by analysis, are generally termed "certified" reference materials. The U.S. Bureau of Standards refers to their known substances as Standard Reference Materials (SRM). Such materials are prepared, tested, and certified by experts in their fields. Thus, these reference materials are suitable for validating both the absolute accuracy and the precision of analytical methods.

Other homogeneous materials can be used to provide data on inter- and intralaboratory precision and relative accuracy. Frequently, a large portion of a single sample, deemed to be representative of the materials being analyzed, will be thoroughly homogenized and split into two or more samples submitted to the laboratories involved.

In addition, if suitable laboratory facilities and expertise are available, portions of a sample can be treated ("spiked") with known amounts of one or more elements or compounds. The "spiked" samples, together with a portion of the original "unspiked" material, are submitted for analysis. The recovery of the added elements or compounds is indicative of the accuracy being achieved.

3. REFERENCE MATERIALS FOR VARIOUS FUEL CATEGORIES

A. Gaseous Fuels

Virtually all gaseous reference mixtures are prepared by blending pure components, both by weight and by volume, rather than analyzing a "real" sample. This approach is practical since the number of possible components in any gaseous fuel is relatively limited, while the range of concentration varies widely according to the source of the gas.

Gaseous fuel standards are available from commercial suppliers in "certified" and "analyzed" grades. A listing of the sources is given in Table A-1.

B. Liquid Fuels

A listing of reference materials available for liquid fuels is given in Table A-2. As can be seen, only a limited number of parameters are covered by available materials. This lack of materials for other parameters has been attributed, for the most part, to the lack of demand. Standards suitable for other parameters, such as nitrogen, can be prepared by "spiking" a low nitrogen oil with one or more appropriate (heterocyclic, aliphatic, etc.) nitrogen compounds. Metals can be added as organometalic complexes. Suitable materials of this nature are available from the National Bureau of Standards (SRM 1051-1080) or from Continental Oil Company, Ponca City, Oklahoma (additives marketed as CONOSTANS®).

C. Solid Fuels

A listing of the reference materials available for solid fuels is given in Table A-3. The principal matrix available is coal, and the number of parameters covered is quite limited. A frequently stated reason for the limited number of coal materials available is that they tend to be unstable due to oxidation. As shown in the listing, a botanical standard for trace elements and nitrogen should be a reasonably close match for the cellulosic fuels, peat and RDSF, in lieu of materials specific to those fuels. "Spiking" solid fuels with additives is more difficult than with liquid fuels since achieving homogeneous distribution takes considerably more time and care. Spiking should only be attempted if the fuel is very finely divided and is easily mixed in a ball or roller mill.

4. SOURCES OF REFERENCE MATERIALS

Sources of the various reference materials are listed on Tables A-1 to A-3. In addition to the National Bureau of Standards, contacts were made with U. S. marketing representatives of European and Japanese standards organizations. Unfortunately, no fuel-related reference materials are available at this time, from any source.

Compounds for "spiking" purposes (nitrogen-containing organics, for example) are available from a number of reliable reagent chemical supply firms, such as Eastman Kodak Company. As noted under Liquid Fuels, organometallic additives are available from Continental Oil Company.

Table A-1

STANDARD REFERENCE MATERIALS FOR GASEOUS FUELS

NUMBER	STANDARD FOR:	DESCRIPTION	SOURCE
GF-1	Natural gas components	Prepared mixture simulating natural gas	PC
GF-2	Gaseous fuel components	Custom-blended mixtures of components can be made up to correspond to any gaseous fuel composition. Mixtures generally available in "primary standard" (highest accuracy) and "working" or "certified standard" grades.	MGP SET

Sources: PC - Philips Chemical Company, Borger, Texas

MGP - Matheson Gas Products, East Rutherford, New Jersey

SET - Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania

Table A-2

STANDARD REFERENCE MATERIALS FOR LIQUID FUELS

NUMBER	STANDARD FOR:	DESCRIPTION	SOURCE
LF-1	S in residual oil	SRM 1621, 1622, 1623 (1.1%, 2.1%, and 0.3% S)	NBS
LF-2	S in distilate oil	SRM 1624 (0.2% S)	NBS
LF-3	Trace elements (Ni, Pb, V, Zn, Fe, S) in residual oil	SRM 1634	NBS
LF-4	Trace Ni and V in residual oil	GM-5 (certified by Western Gas and Oil Association and American Petroleum Institute)	NBS
LF-5	Calorific value	SRM 217b (2,2,4-trimethylpentane, heat of combustion standard) [Also see Table A-3: S-5.]	NBS

Source: NBS - National Bureau of Standards, Office of Standard Reference Materials, Washington, D. C.

Table A-3

STANDARD REFERENCE MATERIALS FOR SOLID FUELS

NUMBER	STANDARD FOR:	DESCRIPTION	SOURCE
SF-1	Ash and S in coal	SRM 1631 (set of 3)	NBS
SF-2	Trace elements (14) in coal	SRM 1632	NBS
SF-3	Trace Hg in coal	STM 1630	NBS
SF-4	N and trace elements (14) in RDSF and peat	SRM 1571 (prepared from leaves)	NBS
SF-5	Calorific value	SRM 39i (benzoic acid, heat of combustion standard)	NBS

Source: NBS - National Bureau of Standards, Office of Standard Reference Materials, Washington, D. C.

APPENDIX B

LABORATORY DIRECTORIES

LABORATORY DIRECTORIES

Given below is a list of laboratory directories which may be of use in obtaining the services of an analytical laboratory for fuel analyses. For listings that cover a specific geographical area, it is suggested that State directories be consulted. The Department of Commerce or its equivalent in most states publishes directories of research organizations and laboratories within the State.

1. The American Council of Independent Laboratories, Inc., Directory, 1976.

   Published by: ACIL
   1725 'K' Street, N. W.
   Washington, D. C.

   (The Directory is revised every two years. The 1978 Directory will be available in early 1978.)

2. Industrial Research Laboratories of the United States, Fourteenth Edition, 1975.

   Published by: R. R. Bowker Company
   1180 Avenue of the Americas
   New York, New York 10036

   (Directory is revised approximately every five years.)

3. Directory of Testing Laboratories, STP 333 C, January, 1973.

   Compiled and published by: American Society for Testing and Materials
   1916 Race Street
   Philadelphia, Pennsylvania 19103

4. Directory of Testing Laboratories, Commerical and Institutional, STP 333 A, November, 1969.

   Compiled and published by: American Society for Testing and Materials
   1916 Race Street
   Philadelphia, Pennsylvania 19103

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5. LABGUIDE 1975-1976, August, 1975. ACS Laboratory Guide to Instruments, Equipment and Chemicals.

Published by: American Chemical Society
115 Sixteenth Street, N. W.
Washington, D. C. 20036

(Pubished annually in August by the ACS.)

6. Union Internationale des Laboratoires Independants, Register of Members, 1975.

Published by: Ashbourne House
Alberon Gardens
London NW11 OBN
England

(Listing covers laboratories in North and South America, Europe, Australia, and other localities.)

APPENDIX C

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR EACH FUEL

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INTRODUCTION

The following tables give typical values, or ranges, of the parameters specified for each of the fuels covered in this manual. The values associated with any range are not necessarily the maximum and minimum values that could be found, but generally delineate a range that most values will be found in.

The sources used in the preparation of a table are listed with each table.

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Table C-1

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR GASEOUS FUELS

PARAMETER	NATURAL GAS	COAL GASES		PETROLEUM GASES	
		Lurgi (O_2)[a]	Koppers-Totzek[b]	Pyrolysis of No. 4 Fuel Oil	Hydrogasification of Heavy Naphtha
Hydrocarbons - mol %					
CH_4 -	93	10-14		24-28	34
C_2H_6/C_2H_4	3.9/0			2-3/18-21	12/9
C_3H_8/C_3H_6	0.7/0			0.3-0.7/2-3	0.4/2
C_4H_{10}/C_4H_8	0.1/0			0/0.7-1.5	0.1/0.5
$> C_4$	0.2			3-4 (some aromatics)	$< 0.1/2-3$
Others - mol %					
CO		25-30	55		
H_2		50-60	35	12-14	40
CO_2	1		7		trace
N_2	0.6	> 0.5	1	30 (inert carrier gas)	
O_2					
H_2S (in mg/cu m)	∿ 1	Sulfide content dependent upon sulfur in feed - may be up to 7,000 mg/cu m for high sulfur (3%) coal.			
Total S (in mg/cu m)	∿ 1				
Calorific Value Btu/scf (K cal/cu m)	1,000 (9,000)	400 (3,600)	300 (2,700)	1,200 (10,700)	990 (8,800)

All notes and sources of information on following page.

Notes for Table C-1:

a. For bituminous coal.
b. For O_2, bituminous coal.

Sources:

1. Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 10: "Gas, Manufactured", Second Edition, Interscience, New York, 1966.

2. Tillman, D. A., "Status of Coal Gasification," Environmental Science Technology, Volume 10, pages 34-38, 1976.

Table C-2

AVERAGE VALUES OF PARAMETERS SPECIFIED FOR PETROLEUM FUELS

	LPG		GASOLINE (BY GRADE)						TURBINE FUELS (BY GRADE)	
PARAMETERS	PROPANE	BUTANE	A	B	C	D	E	AVIATION GASOLINE	TYPE A	TYPE B
1a. Carbon, wt. %	—	—								
1b. Hydrogen, wt. %	—	—								
2. Nitrogen, wt. %	—	—								
3. Sulfur, wt. %			0.1 M	0.1 M	0.1 M	0.1 M	0.1 M	0.05 M	0.055	0.044
4. Oxygen, wt. %	—	—								
5. Chlorine, wt. %	—	—								
6. Water and Sediment		none							0.2	0.1
7. Ash, wt. %	—	—								
8. Calorific Value, Btu/lb.	21560	21180						18720–18800	18600	18700
9. Carbon Residue, wt. %	—	—								
10. Distillation Temperature										
Volume Evaporated:										
10%, °F			158	149	140	131	122	158	369	222
50%, °F			170–250	170–245	170–240	170–235	170–230	221	410	315
90%, °F			374	374	365	365	365	212–257	464	423
End Point			437	437	437	437	437	338	500	480
11. Vapor Pressure, lb.	124 (70°F)	31 (70°F)	9	10	11.5	13.5	15	7.0	—	3 M
12. Flash Point, °F	—	—							110	—
13. Pour Point, °F	—	—						-72 FP	-40	-60
14. Viscosity, Kinematic CS	—	—							8.85	2.94
15. Density, g/cm^3	0.509	0.509							39-51 (API)	45-57 (API)
16. Corrosion, #	1	1	1	1	1	1	1	1	1	1

All notes appear on the last page of this table.

Table C-2

AVERAGE VALUES OF PARAMETERS SPECIFIED FOR PETROLEUM FUELS

(continued)

	DIESEL FUEL (BY GRADE)				HEATING OILS (BY GRADE)					
PARAMETER	1(C-B)	2(T-T)	3(R-R)	4 (S-M)	#1	#2	#4	#5	#6	WASTE OIL
1a. Carbon, wt. %										
1b. Hydrogen, wt. %										
2. Nitrogen, wt. %										
3. Sulfur, wt. %	0.14	0.22	0.29	0.54	0.07	0.25	0.77	1.07	1.33	0.3
4. Oxygen, wt. %										
5. Chlorine, wt. %										
6. Water and Sediment	0.03 M	0.1 M	0.1 M	0.5 M	T	0.1 M	0.5 M	0.16 M	0.15	4.4
7. Ash, wt. %	0.0005	0.0009	0.001	0.0023			0.1 M	0.035	0.41	1.3-1.8
8. Calorific Value, Btu/lb.										
9. Carbon Residue, wt. %	0.057	0.088	0.117	0.163	0.052	0.116	3.3	6.7	10.7	2.2
10. Distillation Temperature										
Volume Evaporated:										
10%, °F	393	430	440	448	390	432	496			
50%, °F	440	490	502	509	437	499	674			
90%, °F	501	557	574	582	550 M	640 M				
End Point	542	600	618	622	533	629	754			
11. Vapor Pressure, lb.										
12. Flash Point, °F	100 Ml	125 Ml	130 Ml	130 Ml	100 Ml	100 Ml	130 Ml	130 Ml	150 Ml	215
13. Pour Point, °F					0 M	20 M	20 M			
14. Viscosity, Kinematic CS	1.84	2.54	2.74	2.79	1.79	2.61	15.4	60.2	—	
15. Density, g/cm^3	42 (API)	37 (API)	35 (API)	34 (API)	43 (API)	35 (API)	21 (API)	17 (API)	12 (API)	25 (API)
16. Corrosion, #	2	3	3	—	3					

LPG: Liquefied Petroleum Gas M: Maximum Specified Value Ml: Minimum Specified Value

T: Trace API: API units - (141.2/sp. gr.) - 131.5

Table C-3

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR SHALE OIL

	TYPICAL RANGE OF VALUES[a]	
PARAMETERS	CRUDE	REFINED
1a. Carbon, wt. %	80 - 85	80 - 85
1b. Hydrogen, wt. %	10 - 12	10 - 12
2. Nitrogen, wt. %	1.2 - 2.4	1.0 - 1.6
3. Sulfur, wt. %	0.5 - 1.0	0.5 - 1.0
4. Oxygen, wt. %	1.5 - 6	1 - 2
5. Chlorine, wt. %	< 0.1	< 0.1
6. Water and Sediment	NA[b]	NA
7. Ash, wt. %	~ 0.06 (?)	< 0.01
8. Calorific Value, Btu/lb. (cal/g)	NA	~ 20,000 (11,000)
9. Carbon Residue, wt. %	1.5 - 5	NA
10. Distillation, Volume % (Typical Values)		
IBP to 400°F	18%	NA
400°F to 600°F	24%	
600°F to 900°F	34%	
900°F + higher	24%	
11. Vapor Pressure	NA	NA
12. Flash Point	NA	NA
13. Pour Point, °C (°F)	4.4 - 32 (40 - 90)	NA
14. Viscosity, SUS at 100°F	50 - 350	NA
15. Density, g/cm^3	0.88 - 0.94	.75 - .9 for distillates
16. Corrosion	NA	NA

NA - Not Available

a. Sources used are listed on the following pages.

b. Typical quantities of "bound water" in crude shale oil produced above-ground retorts may be only a few percent. Crude shale oil from in situ retorting may contain from a few percent to 50 percent distillable water. (See Source #3 on the following page.)

Sources for Table C-3:

1. Van Nostrand's Scientific Encyclopedia, Fifth Edition, 1976, Douglas M. Considine, Editor, Van Nostrand Rinehold Company.

2. Ruberto, R. G., Jewell, D. M., Jensen, R. K., and Cronauer, D. C., "Characterization of Synthetic Liquid Fuels," Shale Oil, Tar Sands, and Related Fuel Sources, Chapter 3. Teh Fu Yen, Editor, Advances in Chemistry Series 151, American Chemical Society, Washington, D. C., 1976.

3. Jackson, L. P., Poulson, R. E. Spedding, T. J., Phillips, T. E., and Jensen, H. B., "Characteristics and Possible Roles of Various Waters Significant to In Situ Oil-Shale Processing," Colorado School of Mines Quarterly, Volume 70, October, 1975, pages 105-134.

4. Jackson, L. P., Morandi, J. R., and Poulson, R. E., "Compositional Variation of Retorted Shale Oils with Stratigraphy: Wyoming Core, Northern Green River Basin," paper presented at the Fuel Chemistry Division Symposium on "Oil Sand and Oil Shale," American Chemical Society Meeting, May 29-June 2, 1977, Montreal, Canada.

5. Poulson, R. E., Smith, J. W., Young, N. B., Robb, W. A., and Spedding, T. J., "Minor Elements in Oil Shale and Oil Shale Products," U. S. Energy Research and Development Administration, Laramie Energy Research Center, Laramie, Wyoming, January, 1977. (Report No. LERC/RI-77/1.)

6. Poulson, R. E., "Nitrogen and Sulfur in Raw and Refined Shale Oils," Division of Fuel Chemistry, American Chemical Society. Preprints Volume 20, No. 2, April 6-11, 1975, pages 183-197.

7. Frost, C. M. and Poulson, R. E., "Nitrogen Types in Syncrudes from In Situ Crude Shale Oil," Division of Fuel Chemistry, American Chemical Society. Preprints Volume 20, No. 2, April 6-11, 1975, pages 176-182.

8. Jensen, H. B., Poulson, R. E., and Cook, G. L., "Characterization of a Shale Oil Produced by In Situ Retorting," Division of Fuel Chemistry, American Chemical Society. Preprints Volume 15, No. 1, March 29-April 2, 1971, pages 133-121.

9. Dinneen, G. V., Ball, J. S., and Thorne, H. M., "Composition of Crude Shale Oils," Industrial and Engineering Chemistry, Volume 44, No. 11, 1952, pages 2362-2365.

10. "Report of the Conference-Workshop entitled 'Analytical Chemistry Pertaining to Oil Shale and Shale Oil'," sponsored by and held at the National Science Foundation, Washington, D. C., June 24-25, 1974.

Sources for Table C-3 (continued):

11. Poulson, R. E., Frost, C. M., and Jensen, H. B., "Characteristics of Synthetic Crude from Crude Shale Oil Produced by In Situ Combustion Retorting," Division of Fuel Chemisty, American Chemical Society. Preprints, Volume 19, No. 2, 1975, pages 175-182.

12. Robinson, W. E. and Cook, G. L., "Compositional Variations of the Organic Matter of Green River Oil Shale - Colorado No. 1 Core," U. S. Department of the Interior, Bureau of Mines Report of Investigations No. 7492, 1971.

13. Robinson, W. E. and Cook, G. L., "Compositional Variations of the Organic Material from Green River Oil Shale - Wyoming No. 1 Core," U. S. Department of the Interior, Bureau of Mines Report of Investigations No. 7280, 1973.

14. Ruark, J. R., Sohns, H. W., and Carpenter, H. C., "Gas Combustion Retorting of Oil Shale Under Anvil Points Lease Agreement: Stage II," U. S. Department of the Interior, Bureau of Mines Report of Investigations No. 7540, 1971.

15. "Fuel Contaminants - Volume 1: Chemistry," U. S. Environmental Protection Agency, Research Triangle Park, Durham, North Carolina, 1976. (Report No. EPA-600/2-76-177a.)

Table C-4

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR COAL LIQUIDS

PARAMETER	TYPICAL RANGE OF VALUES [a]
1a. Carbon (Total), wt. %	80 - 90
1b. Hydrogen, wt. %	5 - 10
2. Nitrogen, wt. %	0.1 - 2.5
3. Sulfur, wt. %	< .1 - 3.0
4. Oxygen, wt. %	0.1 - 12
5. Chlorine, wt. %	< 0.1
6. Water and Sediment, wt. %	< 5
7. Ash, wt. %	0.1 - 1.0
8. Calorific Value, Btu/lb. (cal/g)	15,000 - 20,000 (8,330 - 11,100)
9. Carbon Residue, wt. %	NA
10. Distillation, Volume % (Typical Values)	
IBP to 400°F	10% - 20%
400°F to 600°F	20% - 50%
600°F to 900°F	20% - 50%
900°F + higher	10% - 20%
11. Vapor Pressure	NA
12. Flash Point	NA
13. Pour Point, °C (°F)	< 38 (< 100)
14. Viscosity, SUS at 100°F	NA
15. Density	0.85 - 1.2
16. Corrosion	NA

NA - Not Available

[a] Sources used are listed on the following page.

Sources for Table C-4:

1. Cusumano, J. A., DallaBetta, E. A., and Levy, R. B., "Scientific Resources Relevant to the Catalytic Problems in the Conversion of Coal," ERDA FE-2017-1, October, 1976.

2. Whitehurst, D. D., Farcasiu, M., and Mitchell, T. O., "The Nature and Origin of Asphaltenes in Processed Coals," Mobil Research and Development Corporation, Princeton, New Jersey.

3. Yen, T. F., Shale Oil, Tar Sands, and Related Fuel Sources, American Chemical Society, Washington, D. C., 1976.

4. Work in progress at Arthur D. Little, Inc., under ERDA contract no. EX-76-C-01-1754, "Experimental Study of an Extracting Coking Process to Produce Low-Sulfur Liquid Fuels from Bituminous Coal."

Table C-5

TYPICAL VALUES OF PARAMETERS SPECIFIED FOR METHYL FUEL ANALYSIS

PARAMETER	APPROXIMATE OR ESTIMATED VALUE
Methanol Content, wt. %	90 - 95
1. Nitrogen	?, probably small
2. Sulfur	?, probably very small (< 1 ppm)
3. Chloride	?, present only if shipped by ocean tanker
4. Water, wt. %	0.5 - 5
5. Higher Alcohols, wt. %	0.1 - 10
6. Nonvolatile Matter, wt. %	∿ 0.01
7. Calorific Value, Btu/lb. (cal/g)	10,000 (5,550)
8. Specific Gravity (20°C/20°C)	0.80 - 0.82
9. Viscosity, cp (25°C)	0.67 - 0.79
10. Boiling Point, °C (1 atm.)	65 - 67
11. Flash Point, °C	11 - 13 (closed cup) 18 - 21 (open cup)
12. Vapor Pressure, mm Hg (20°C)	75 - 90
13. Corrosion Rate	?
14. Acidity, wt. % as acetic acid	∿ 0.015

Sources:

1. Personal communications with Stanley Dale and Douglas Shooter, Arthur D. Little, Inc.
2. Manufacturer's data sheets for methanol.
3. Carr, C., and Riddick, J. A., "Physical Properties of Methanol-Water Systems," Industrial Engineering Chemistry, 43, pages 692-696, 1951.

Table C-6

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR COAL AND COKE

PARAMETER	TYPICAL RANGE OF VALUES (MAF BASIS)	
	COAL	COKE
1a. Carbon (Total), wt. %	60. - 95.	90 - 95[a]
1b. Hydrogen, wt. %	2.9 - 5.6	1 - 2[a]
2. Nitrogen, wt. %	0.5 - 2.1	NA
3. Sulfur, wt. %	0.25 - 5.0	0 - 10
4. Oxygen, wt. %	2.0 - 35.0	NA
5. Chlorine, wt. %	< 0.5	Trace
6. Moisture, wt. %	1.0 - 50.0	0.5 - 5.0
7. Volatile Matter, wt. %	3.5 - 60.	0.5 - 6.0
8. Ash, wt. %	5.0 - 20.0	0.5 - 20
9. Calorific Value, Btu/lb. (cal/g)	8,000 - 16,000 (4,440 - 8,880)	12,000 - 16,000 (6,660 - 8,880)

NA - Not Available

[a] Rough estimate only.

Sources:

1. *Steam, Its Generation and Use*, The Babcock and Wilcox Company, New York, New York, 1963.
2. Kirk-Othmer, *Encyclopedia of Chemical Technology*, Second Edition, Volume 5, 1967, page 627.
3. Mezey, E. J., Singh, S., and Hissong, D. W., "Fuel Contaminants: Volume 1 - Chemistry," EPA-600/2-76-177a, July, 1976.

Table C-7

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR REFUSE-DERIVED SOLID FUELS (RDSF)

(Values applicable to municipal RDSF)

PARAMETER	TYPICAL RANGE OF VALUES (DRY BASIS)[a]
1a. Carbon (Total), wt. %	35 - 50
1b. Hydrogen, wt. %	5 - 7
2. Nitrogen, wt. %	0.3 - 1.5
3. Sulfur, wt. %	0.1 - 0.7
4. Oxygen, wt, %	30 - 40
5. Chlorine, wt, %	0.1 - 1.0
6. Moisture, wt. %	1 - 5 (as fired basis) for some highly processed RDSF 25 - 55 (as fired basis) for RDSF that has not been dried or chemically treated
7. Volatile Matter, wt. %	35 - 90
8. Ash, wt. %	5 - 35
9. Ash Fusibility, C°	

	Reducing Atmosphere[b]	Oxidizing Atmosphere[b]
Initial deformation	1030 - 1130	1110 - 1150
Softening (H = W)	1200 - 1290	1240 - 1300
Softening (H = 1/2W)	1210 - 1310	1250 - 1340
Fluid	1320 - 1400	1360 - 1480

10. Apparent Density, lbs./ft.^{3} (g/cm^3)	10 - 40 (0.24 - 0.56)
11. Sieve Analysis	(Average particle size may range from 0.01 cm for highly processed RDSF up to 2 cm for others.)
12. Calorific Value, Btu/lb. (cal/g)	4,000 - 8,500 (2,200 - 4,700)
13. Carbonate Carbon	NA

NA- Not Available

a. Sources used are listed on the following page.

b. From Source #4; data are from three samples of St. Louis Refuse, with magnetic metals removed.

Sources for Table C-7:

1. Schultz, J., Sullivan, P. M., and Walker, F. E., "Characterizing Combustible Portions of Urban Refuse for Potential Use as Fuel," U. S. Department of the Interior, Bureau of Mines Report of Investigations, RI 8044, 1975.

2. Solid Wastes: Origin, Collection, Processing, and Disposal, C. L. Mantell, Editor, John Wiley and Sons, New York, 1975.

3. "Report of Analyses for Union Electric Company," St. Louis Missouri, by Research 900, Division of Ralston-Purina Company, St. Louis, Missouri. Unpublished data from December, 1973, through June, 1974.

4. Handbook of Solid Waste Disposal, Materials and Energy Recovery, Pavoni, J. L., Heer, J. E., Jr., and Hagerty, D. S., Van Nostrand Reinhold Company, New York, 1975.

5. "Power Boilers: The Ultimate Solution for Solid Waste?", Spaite, P. and Miller, C., Power Engineering, Volume 76 (No. 3), pages 54-55, March, 1972.

6. "Specifications for Materials Recovered from Municipal Refuse," Alter, H. and Reeves, W. R.; Report to the U. S. Environmental Protection Agency, Cincinnati, Ohio, May, 1975. (EPA-670/2-75-034.)

7. Personal communication from Thomas Lamb, Arthur D. Little, Inc., March, 1977.

Table C-8

TYPICAL VALUES (RANGES) OF PARAMETERS SPECIFIED FOR PEAT

PARAMETER	TYPICAL RANGE OF VALUES (DRY BASIS)
1a. Carbon (Total), wt. %	45 - 60
1b. Hydrogen, wt%	3.5 - 6.8
2. Nitrogen, wt. %	0.75 - 3.0
3. Sulfur, wt. %	$\sim$ 0.3
4. Oxygen, wt. %	20 - 40
5. Chlorine, wt. %	$\lesssim$ 0.1
6. Moisture, wt. %	70 - 90 (as found) 30 - 50 (air dried)
7. Organic Matter, wt. %	45 - 75
8. Ash, wt. %	$\sim$ 10
9. Ash Fusibility	NA
10. Apparent Density	NA
11. Sieve Analysis	NA
12. Calorific Value, Btu/lb. (cal/g)	7,500 - 9,600 (4,200 - 5,300)
13. Carbonate Carbon	NA

NA - Not Available

Sources:

1. Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, 1967. (See article on "Coal," Volume 5, page 627.)
2. Van Nostrand's Scientific Encyclopedia, Fifth Edition, 1976, Douglas M. Considine, Editor, Van Nostrand Rinehold Company.
3. Analyses of peat by Arthur D. Little, Inc. See Appendix D.

APPENDIX D

RESULTS OF FUEL ANALYSIS TESTS

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1. INTRODUCTION

The Contractor (Arthur D. Little, Inc.), in conjunction with four analytical service laboratories, undertook a number of fuel analyses - primarily on uncommon fuel materials - for a variety of reasons. It was expected that the analyses conducted on the uncommon fuels would, if successful, lend some support to a statement of applicability for the method chosen and used, and it was expected that a comparison of the inter- and intralaboratory precision would yield some insight - if not valid data - on the precision of the method, as applied to the fuel in question. Finally, the results of the analyses were of general interest (1) to confirm literature data on the range of values to be expected, or (2) to give values not obtained from the literature.

2. ANALYSES CONDUCTED

Samples of shale oil, coal liquid, No. 4 fuel oil, waste lubricating oil, processed municipal refuse, and peat were sent to three laboratories who were asked to analyze - in duplicate - for sulfur, nitrogen, chlorine, ash, heat of combustion, and (for the two solid fuels) moisture and organic matter. The methods specified are shown in Table D-1. Some variability of the methods used for the nitrogen and sulfur analyses had to be accepted because one or more of the laboratories did not perform the specified methods. The methods in Table D-1 were selected very early in the course of this project in order to allow sufficient time for completion of the analyses and, in some cases, are not the preferred method given in this report.

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The analyses were conducted in the period between March 1977, and May 1977.

3. DESCRIPTION OF FUELS

A. No. 4 Fuel Oil

A sample of this commercial grade oil was obtained from the Contractor's facilities on March 16, 1977, at a point just prior to the inlet to a boiler. The tanks in which the fuel was stored had been recently cleaned.

B. Coal Liquids

A sample of coal liquid (7.0% hydrogen) was obtained from a commercial source. The material is derived from a solvent-refined coal process. This is an extractive process in which a petroleum-based donor liquid is placed in contact with coal under hydrogen pressure resulting in an extracted coal oil.

C. Shale Fuel Oil

A sample of a shale oil distillate was obtained from a private source. The grade of the distillate was intended to be suitable for use as a turbine fuel for aircraft. The shale fuel oil was produced in a special run and should not be considered typical of all shale oil distillate.

D. Waste Lubricating Oil

A sample of waste lubricating oil (from automobile crank cases) was obtained from a service garage in Cambridge, Massachusetts, on March 8, 1977.

E. Milled Peat

A sample of garden-grade peat was obtained from a commercial source in March, 1977. The peat container specified the contents to be "pure" Canadian Sphagnum Peat Moss. Because of the excessively fibrous and inhomogeneous nature of the peat, it was milled (in a ball mill) prior to shipment to the analytical laboratories.

F. Processed Municipal Refuse

A sample of processed municipal refuse was obtained from a private source on March 7, 1977. The material is produced by subjecting raw municipal refuse to the following series of operations: size reduction, magnetic separation, screening, chemical treatment, milling, and, final screening. This is a more highly processed fuel than is prepared at many locations and may, therefore, not be representative of refuse-derived solid fuels.

4. DISCUSSION OF RESULTS

The results of the analyses are given in the following section. The results from two laboratories agreed, in most cases, within the reproducibility limits for the method. These two laboratories also had generally good precision on the duplicate analyses carried out for each parameter. Laboratory #3 was "off" in some data, did not carry out many of the required solid fuel analyses, and did not perform duplicate analyses. The problems associated with this laboratory, though significant, could not be corrected within the timeframe of this study; their results are included here, in part, to demonstrate the variability of results that may be obtained from different laboratories.

Significant discrepancies can be seen in the results for peat and, to a much lesser extent, for the processed municipal refuse. It is thought that differences in drying techniques (leading, possibly, to insufficient drying) may be the root cause of the differences in the peat analyses by laboratories #1 and #2. The outer (cardboard) peat container was received by laboratory #2 in a damaged condition, though the inner plastic bag containing the sample was not broken. Still, some loss of moisture may have occurred in shipping. These results clearly indicate the importance of sealed sample containers where moisture determinations are required, and the importance of thorough drying for samples containing significant amounts of water (e.g., peat, refuse-derived solid fuels, crude shale oils, etc.).

5. RESULTS FOR N, S, Cl, ASH, HEAT OF COMBUSTION MOISTURE, AND ORGANIC MATTER

The results for N, S, Cl, ash, heat of combustion, moisture, and organic matter for the six fuels are given in Tables D-2 through D-7.

Table D-1

ASTM METHODS SUGGESTED BY CONTRACTOR TO BE USED FOR INDICATED ANALYSES

SAMPLE	NITROGEN	SULFUR	CHLORINE	ASH	MOISTURE	ORGANIC MATTER	HEAT OF COMBUSTION (BTU)
Liquid Coal	D 3228-73	D 1266-70 with 10:1 dilution with sulfur free solvent	D 808-63	D 482-74 and D 874-72	---	---	D 240-76
Shale Oil	D 3228-73	D 1266-60 with 10:1 dilution with sulfur free solvent	D 808-63	D 482-74 or D 874-72	---	---	D 240-76
No. 4 Fuel Oil	D 3228-73	D 1552-64	D 808-63	D 482-74 and D 874-72			D 240-76
Waste Lubricating Oil	D 3228-73	D 1552-64	D 808-63	D 482-74 and D 874-72	---	---	D 240-76
Processed Municipal Waste	D 2973-71	D 3177-73 Bombwashing Method	D 2361-66	D 2974-71	D 2974-71 (Method II)	D 2974-71	D 2015-66 or D 3286-73
Peat	D 2973-71	D 3177-73 Bombwashing Method	D 2361-66	D 2974-71	D 2974-71 (Method II)	D 2974-71	D 2015-66 or D 3286-73

Table D-2

ANALYSES OF COAL LIQUID

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		NOTES
		DUPLICATES	AVERAGE	
Nitrogen, wt. % (D 3228-73)	1	0.85, 0.82,	0.84	
	2	0.81, 0.83	0.82	
	3	0.31	(0.31)	Lab #3 used Perkin-Elmer 240
	Average		0.83	Average excludes results from Lab #3
Sulfur, wt. % (D 1552-64)	1	0.60, 0.54	0.57	
	2	0.50, 0.51	0.51	
	3	0.53	0.53	
	Average		0.54	
Chlorine, wt. % (D 808-63)	1	0.01, 0.04	0.03	
	2	< 0.1, < 0.1	< 0.1	
	3	"trace"	--	
	Average		--	
Ash, wt. % (D 482-74, dry)	1	< .001, < .001	< .001	
	2	< .01, < .01	< .01	
	3	0.003	0.003	
	Average		--	
Ash, wt. % (D 874-72, sulfated)	1	< .001, < .001	< .001	
	2	< .01, < .01	< .01	
	3	NA	--	
	Average		--	
Heat of Combustion, Btu/lb (D 240-76)	1	16,914; 16,926	16,920	
	2	16,920; 16,882	16,901	
	3	20,895	(20,895)	
	Average		16,910	Average excludes results from Lab #3

Table D-3

ANALYSES OF SHALE FUEL OIL

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		NOTES
		DUPLICATES	AVERAGE	
Nitrogen, wt. % (D 3228-73)	1	0.29, 0.27	0.28	
	2	0.25, 0.25	0.25	
	3	0.52	(0.52)	Lab #3 used Perkin-Elmer 240
	Average		0.26	Average excludes results from Lab #3
Sulfur, wt. % (D 1552-64)	1	0.54, 0.53	0.54	
	2	0.47, 0.48	0.48	
	3	0.54	0.54	
	Average		0.52	
Chlorine, wt. % (D 808-63	1	0.05, 0.04	0.05	
	2	< 0.1, < 0.1	< 0.1	
	3	"none"	--	
	Average		--	
Ash, wt. % (D 482-74, dry)	1	< .001, < .001	< .001	
	2	< .01, < .01	< .01	
	3	0.001	0.001	
	Average		--	
Ash, wt. % (D 874-72 sulfated)	1	< .005, < .002	< .004	
	2	< .01, < .01	< .01	
	3	NA	--	
	Average		--	
Heat of Combustion, Btu/lb (D 240-76)	1	19,323; 19,292	19,308	
	2	19,298; 19,315	19,307	
	3	19,269	19,269	
	Average		19,295	

Table D-4

ANALYSES OF NO. 4 FUEL OIL

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		NOTES
		DUPLICATES	AVERAGE	
Nitrogen, wt. % (D 3228-73)	1	"none detected"		
	2	0.12, 0.12	0.12	
	3	0.10	0.10	Lab #3 used Perkin-Elmer 240
	Average		0.11	
Sulfur, wt. % (D 1552-64)	1	0.42, 0.45	0.44	
	2	0.43, 0.45	0.44	
	3	0.44	0.44	
	Average		0.44	
Chlorine, wt. % (D 808-63)	1	0.00, 0.04	0.02	
	2	< 0.1, < 0.1	< 0.1	
	3	"trace"	--	
	Average		--	
Ash, wt. % (D 482-74, dry)	1	< .001, < .001	< .001	
	2	0.02, 0.02	0.02	
	3	0.01	0.01	
	Average		∿ 0.01	
Ash, wt. % (D 874-72, sulfated)	1	< .001 < .001	< .001	
	2	0.02, 0.03	0.03	
	3	NA	--	
	Average		--	
Heat of Combustion, Btu/lb (D 240-76)	1	19,162; 19,165	19,164	
	2	19,233; 19,207	19,220	
	3	19,197	19,197	
	Average		19,194	

Table D-5

ANALYSES OF WASTE LUBRICATING OIL

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS DUPLICATES	AVERAGE	NOTES
Nitrogen, wt. % (D 3228-73)	1	"none detected"	--	
	2	0.06, 0.06	0.06	
	3	0.28	0.28	Lab #3 used Perkin-Elmer 240
	Average		--	
Sulfur, wt. % (D 1552-64)	1	0.41, 0.38	0.40	
	2	0.37, 0.36	0.37	
	3	0.38	0.38	
	Average		0.38	
Chlorine, wt. % (D 808-63)	1	0.19, 0.20	0.20	
	2	0.23, 0.22	0.23	
	3	0.22	0.22	
	Average		0.22	
Ash, wt. % (D 482-74, dry)	1	1.35, 1.34	1.35	
	2	1.35, 1.33	1.34	
	3	1.27	1.27	
	Average		1.32	
Ash, wt. % (D 874-72, sulfated)	1	1.24, 1.49	1.37	
	2	1.60, 1.51	1.56	
	3	NA	--	
	Average		1.47	
Heat of Combustion, Btu/lb (D 240-76)	1	18,917; 18,963	18,940	
	2	19,077; 19,052	19,065	
	3	18,911	18,911	
	Average		18,972	

Table D-6

ANALYSES OF PROCESSED MUNICIPAL REFUSE

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		"DRY" BASIS		NOTES
		DUPLICATES	AVERAGE	DUPLICATES	AVERAGE	
Nitrogen, wt. %						
(D 3179-73)	1	0.40, 0.42	0.41	0.43, 0.41	0.42	
(D 2973-71)	2		--	0.34, 0.34	0.34	
(D 2973-71)	3	< 0.01	--		--	Lab #3 used Perkin-Elmer 240
	Average		--		0.38	
Sulfur, wt. %	1	0.60, 0.51	0.56	0.62, 0.53	0.58	
(D 3177-73,	2		--	0.58, 0.55	0.57	
Bombwashing)	3	NA	--		--	
	Average		--		0.58	
Sulfur, wt. %	1	0.60, 0.55	0.58	0.62, 0.57	0.60	
(D 3177-73,	2	NA	--	NA	--	
Eschka Fusion)	3	NA	--		--	
	Average		--		--	
Chlorine, wt %	1	0.48, 0.48	0.48	0.49, 0.49	0.49	
(D 2361-66)	2		--	0.22, 0.25	0.24	
	3	NA	--		--	
	Average		--		--	
Ash, wt. %	1	14.02, 14.04	14.03	14.44, 14.46	14.45	
(D 2974-71)	2		--	14.0, 13.9	14.0	
	3	13.98	--		--	
	Average		--		14.2	
Moisture, wt. % (D 2974-71, Method II)	1	2.89, 2.90	2.90		--	Air dried moisture = 0.00%
	2	3.39. 3.42	3.41		--	
	3	NA	--		--	
	Average		3.2		--	

Table D-6

ANALYSES OF PROCESSED MUNICIPAL REFUSE (continued)

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		"DRY" BASIS		NOTES
		DUPLICATES	AVERAGE	DUPLICATES	AVERAGE	
Organic Matter, wt. % (D 2974-71)	1	83.08, 83.06	83.07		--	
	2	82.6, 82.7	82.7		--	
	3	NA	--		--	
	Average		82.9		--	
Heat of Cumbustion, Btu/lb (D 2015-66)	1	8,149; 8,098	8,124	8,393; 8,340	8,367	
	2		--	8,365; 8,344	8,355	
	3	NA	--		--	
	Average		--		8,361	

NA - Analysis not done

Table D-7

ANALYSES OF MILLED PEAT

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		"DRY" BASIS		NOTES
		DUPLICATES	AVERAGE	DUPLICATES	AVERAGE	
Nitrogen, wt. %						
(D 3179-73)	1	0.56, 0.55	0.56	2.05, 2.00	2.03	
(D 2973-71)	2		--	0.92, 0.92	0.92	
(D 2973-71)	3	0.05	--		--	Lab #3 used Perkin-Elmer 240
	Average		--		1.5	
Sulfur, wt. % (D 3177-73, Bombwashing)	1	0.10, 0.08	0.09	0.36, 0.30	0.33	
	2		--	0.32, 0.27	0.30	
	3	NA	--		--	
	Average		--		0.32	
Sulfur, wt. % (D 3177-73, Eschka Fusion)	1	0.06, 0.08	0.07	0.23, 0.28	0.26	
	2		--	NA	--	
	3	NA	--		--	
	Average		--		--	
Chlorine, wt. % (D 2361-66)	1	0.02, 0.02	0.02	0.09, 0.09	0.09	
	2		--	< 0.1, <0.1	< 0.1	
	3	NA	--		--	
	Average		--		--	
Ash, wt. % (D 2974-71)	1	2.76, 2.51	2.64	10.10, 9.21	9.66	
	2		--	5.12, 5.68	5.40	
	3	2.72	2.72		--	
	Average		2.68		7.5	
Moisture, wt. % (D 2974-71,	1	53.15, 53.03	53.09		--	Air dried moisture = 41.8% (Lab #1)
	2	(12.7, 12.6)*	(12.7)		--	
	3	NA	--		--	
	Average		--		--	

All notes on following page.

Table D-7

ANALYSIS OF MILLED PEAT (continued)

PARAMETER (METHOD USED)	LAB NUMBER	"AS-RECEIVED" BASIS		"DRY" BASIS		NOTES
		DUPLICATES	AVERAGE	DUPLICATES	AVERAGE	
Organic Matter, wt. % (D 2974-71)	1	44.15, 44.40	44.28		--	
	2	82.2, 81.8	82.0		--	
	3	NA	--		--	
	Average		--		--	
Heat of Combustion, Btu/lb (D 2015-66)	1	3,837; 3,939	3,888	14,055; 14,428	14,242	
	2		--	8,052; 8,083	8,068	
	3	NA	--		--	
	Average		--		--	

NA - Analyses not done

*Sample possibly air dried before analysis due to tear in container during shipment to lab.

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